

The role of tetraalkylammonium salts in the electroreduction of ketones, part II. : the reduction of acetophenone in an aprotic environment

Citation for published version (APA):

Tilborg, van, W. J. M., Smit, C. J., & Santen, van, R. A. (1979). The role of tetraalkylammonium salts in the electroreduction of ketones, part II. : the reduction of acetophenone in an aprotic environment. *Recueil des Travaux Chimiques des Pays-Bas*, 98(11), 526-531. <https://doi.org/10.1002/recl.19790981103>

DOI:

[10.1002/recl.19790981103](https://doi.org/10.1002/recl.19790981103)

Document status and date:

Published: 01/01/1979

Document Version:

Publisher's PDF, also known as Version of Record (includes final page, issue and volume numbers)

Please check the document version of this publication:

- A submitted manuscript is the version of the article upon submission and before peer-review. There can be important differences between the submitted version and the official published version of record. People interested in the research are advised to contact the author for the final version of the publication, or visit the DOI to the publisher's website.
- The final author version and the galley proof are versions of the publication after peer review.
- The final published version features the final layout of the paper including the volume, issue and page numbers.

[Link to publication](#)

General rights

Copyright and moral rights for the publications made accessible in the public portal are retained by the authors and/or other copyright owners and it is a condition of accessing publications that users recognise and abide by the legal requirements associated with these rights.

- Users may download and print one copy of any publication from the public portal for the purpose of private study or research.
- You may not further distribute the material or use it for any profit-making activity or commercial gain
- You may freely distribute the URL identifying the publication in the public portal.

If the publication is distributed under the terms of Article 25fa of the Dutch Copyright Act, indicated by the "Taverne" license above, please follow below link for the End User Agreement:

www.tue.nl/taverne

Take down policy

If you believe that this document breaches copyright please contact us at:

openaccess@tue.nl

providing details and we will investigate your claim.

In a previous paper² the suggestion was made that in the phosphite triester **6** the geometry of the ribopyranoside ring would deviate from the chair configuration. The crystal data now clearly show that the chair configuration is still maintained. A similar situation is established for **7**. Still there is one interesting difference which is visualized in the deviation of the angles of the ribopyranoside ring with respect to the normal tetrahedral angles. In compound **7** this deviation is less pronounced than in **6**.

Experimental

Phosphite triester of methyl β -D-ribopyranoside (**6**)^{2,6}

A mixture of methyl β -D-ribopyranoside (49.2 g = 0.3 mol), trimethyl phosphite (40.9 g = 0.33 mol) and triethylamine (3 drops) was heated with stirring for 48 h in a 150 ml flask equipped with a Vigreux column, condenser, receiver, and a drying tube filled with phosphorus pentoxide. During this period methanol (29 g = 0.9 mol) was collected.

The residue was distilled *in vacuo*. Yield: 54 g (0.281 mol = 94%) of the phosphite triester of methyl β -D-ribopyranoside, b.p. 82–84°C/0.1 mm. It has been crystallized from sodium-dried hexane: colourless needles, m.p. 34.5–35°C.

Thiophosphate O,O,O-triester of methyl β -D-ribopyranoside (**7**)

A mixture of the phosphite triester of methyl β -D-ribopyranoside (8 g = 0.411 mol) and sulphur (1.32 g = 0.0412 mol) was heated in a Carius tube at 170–175°C. The product was shaken with ether (300 ml) and decolourizing carbon (0.3 g) and filtered. The filtrate was evaporated to 75 ml whereupon a nearly colourless compound (4.7 g) crystallized. From the mother liquor another 0.5 g was obtained. The product was recrystallized from ether using some decolourizing carbon. Yield: 5.0 g (0.022 mol = 54%) of colourless crystals, m.p. 101–101.5°C. C₆H₉O₅PS (224.18): calcd. C, 32.15; H, 4.05; found C, 32.4; H, 4.1.

Phosphate triester of methyl β -D-ribopyranoside (**8**)^{4,5}

An ozone-oxygen stream* (dried beforehand with Drierite and calcium chloride) was passed into a solution of the phosphite triester of methyl β -D-ribopyranoside (4.7 g = 0.024 mol) in dry methylene chloride cooled to –75°C until a slight blue colour of excess ozone was apparent in the solution. The off-gases were passed through a trap containing neutral potassium iodide solution. The reaction mixture was then sparged with nitrogen to carry excess ozone into the trap. The cold solution of the adduct (³¹P NMR: = –30.5 ppm upfield from H₃PO₄, clearly pointing to a penta-coordinated phosphorus intermediate) was warmed to 20°C over about 1 h.

Evolution of singlet oxygen proceeded smoothly beginning at about –20°C. The phosphate formed was insoluble in methylene chloride and most other solvents. It was collected and dried *in vacuo* at 100–105°C without further purification. Yield: 4.9 g (0.02355 mol = 98%) of a colourless, crystalline powder decomposing at ~190–195°C. C₆H₉O₆P (208.10): calcd. C, 34.63; H, 4.36; found C, 34.4; H, 4.5.

Acknowledgements

The authors thank Dr. G. J. Visser for the computer drawings and Mr. P. L. M. van den Bosch for carrying out the micro-analyses.

* Oxidation with HgO³ was not successful.

³ L. Keay and E. M. Crook, *J. Chem. Soc.* 710 (1961).

⁴ Q. E. Thompson, *J. Am. Chem. Soc.* **83**, 845 (1961).

⁵ A. P. Schaap, *J. Org. Chem.* **40**, 1185 (1975).

⁶ W. S. Wadsworth and W. D. Emmons, *J. Am. Chem. Soc.* **84**, 610 (1962).

The role of tetraalkylammonium salts in the electro-reduction of ketones. Part II. The reduction of acetophenone in an aprotic environment

W. J. M. van Tilborg, C. J. Smit and R. A. van Santen

*Koninklijke/Shell-Laboratorium, Amsterdam (Shell Research B.V.)
(Received March 2nd, 1979)*

Abstract. A polarographic study of the electro-reduction of acetophenone in dry acetonitrile has revealed that under strictly anhydrous conditions the carbonyl compound can be reduced only if tetraalkylammonium ions are present. The role played by these ammonium ions is discussed. It is concluded that the catalytic effect of the ammonium ions has to be related to an increased polarization of the carbonyl double bond being induced during collision of the ammonium ions with the carbonyl compound. At high ammonium ion concentrations, however, the effect of this catalysis becomes smaller due to preferential adsorption of the ammonium ions on the electrode surface, as a result of which the carbonyl compound is displaced from the direct vicinity of the electrode.

Introduction

In a previous study¹ we have discussed the effect of the presence of tetraalkylammonium ions on the electro-reduction of carbonyl compounds in aqueous media. This study revealed that (a) at its reduction potential the carbonyl

species is not adsorbed on the electrode surface, (b) that at this potential, in the presence of tetraalkylammonium ions,

¹ W. J. M. van Tilborg, L. J. G. Dekker and C. J. Smit, *Recl. Trav. Chim. Pays-Bas*, **97**, 321 (1978).

the mercury electrode is covered with an ammonium ion adsorbate layer and the carbonyl species is reduced – in a diffusion-limited process – on top of that layer, and (c) that there is hardly any interaction between the carbonyl species and the adsorbed ammonium ions.

From the literature² it is known that the electro-reduction of carbonyl compounds in protic media is catalysed by protonation of, or hydrogen bridge formation with the carbonyl group, which enhances its polarization and facilitates the electron transfer. We were greatly interested in the course this electro-reduction would take in an aprotic environment (where the complete absence of protons precludes their catalytic action), particularly because we had found³ that the product composition in the electro-reduction of acetophenone changes from entirely alcoholic into exclusively pinacol-like on changing the medium from protic to aprotic. In addition it had been observed that chiral conducting salts in a protic medium induce asymmetry in the alcohol but not in the pinacol, whereas in an aprotic environment a substantial asymmetric induction in the pinacol occurs⁴. These phenomena point to different mechanisms taking place in the reduction of carbonyl compounds in protic and aprotic media. Since, in the literature, little is known about the electro-reduction of ketones in strictly anhydrous media, we thought it worthwhile to make a study of this type of reaction.

Results and discussion

Reduction of acetophenone in the presence of tetraalkylammonium salts

In an aqueous medium acetophenone is reduced in a two-electron wave at a potential of -1.56 V vs SCE. In dry acetonitrile, this wave is split into two one-electron waves (*vide infra*), positioned at a more negative potential* (Table I, Fig. 1). The positions of the two waves depend on the nature of the anion of the tetraalkylammonium conducting salt. If the reduction is carried out without rigorous exclusion

Table I—Reduction of acetophenone (1.5×10^{-2} mol/l) in the absence of lithium salts. Potentials in V vs SCE.

Conducting salt, 0.05 mol/l	$E_{\frac{1}{2}}^1$	$E_{\frac{1}{2}}^2$
TEAF	-1.76	-2.30
TEACl	-1.95	-2.47
TEAClO ₄	-2.03	-2.52

Table II Reduction of acetophenone (1.5×10^{-2} mol/l) in the presence of lithium salts. Potentials V vs SCE.

Conducting salt	Concentration mol/l	Lithium wave	Acetophenone waves	
			$E_{\frac{1}{2}}^1$	$E_{\frac{1}{2}}^2$
LiF	$0 < 0.05^a$	absent	absent	absent
LiCl	$0 < 0.05^a$	-2.0 ^c	b	b
LiClO ₄	0.05	-2.05 ^c	b	b
TEAF	0.025	absent	-1.77	-2.31
LiF	0.025 ^a			
TEAClO ₄	0.025			
LiF	0.025 ^a	absent	-2.02	-2.56
TEAF	0.028			
LiClO ₄	0.025			
TEACl	0.025	-2.10	b	b
LiCl	$< 0.025^a$			
TEAClO ₄	0.025			
LiClO ₄	0.025	-2.05	b	b

^a saturated solution.

^b if present, masked by the intense lithium reduction peak.

^c Identical waves are observed in the absence of acetophenone.

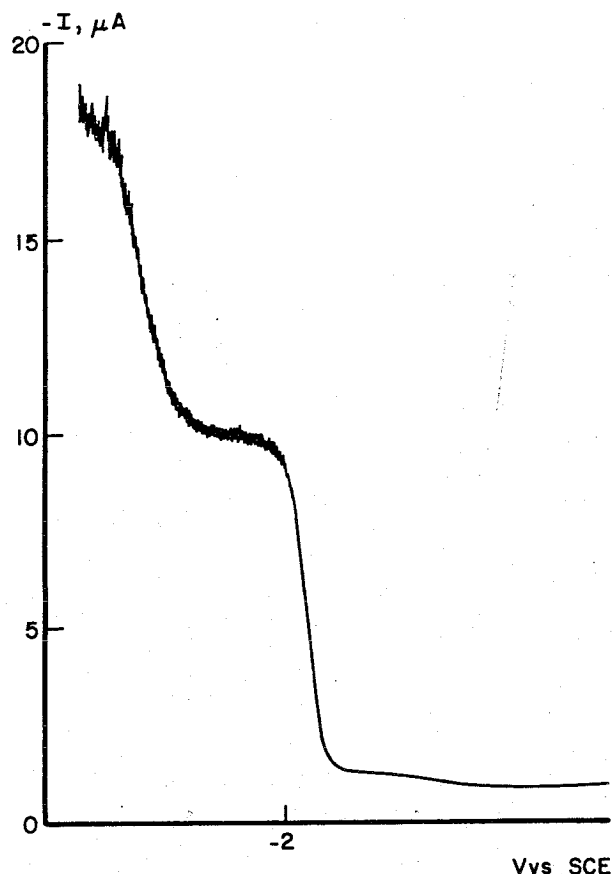


Fig. 1. Polarographic reduction of acetophenone in dry acetonitrile in the presence of tetraethylammonium perchlorate as conducting salt.

of water, one observes an additional, proton-catalysed reduction peak (in the presence of tetraethylammonium chloride, TEACl, appearing at -1.78 V) and an intense proton-reduction peak at a potential more negative than -2.2 V. The latter peak completely masks the second reduction wave of acetophenone.

Reduction of acetophenone in the presence of lithium salts

In the literature, a number of investigators^{5,6} made use of alkali metal salts as the conducting salts in their studies of the electro-reduction of carbonyl compounds. This practice, however, introduces a serious complication as amalgam formation is known⁷ to occur at the strongly negative potentials applied in these reductions. Under these conditions the electro-reduction might change into an amalgam-type reduction of the substrate. We have studied the effect of using different lithium salts as the conducting salts on the electro-reduction of acetophenone (Table II). In the absence

* Cyclic voltammetry at a mercury drop electrode suggests this reduction to be nonreversible. No re-oxidation peak could be observed, even at scan rates as high as 100 Vs⁻¹.

² P. J. Elving and J. T. Leone, J. Am. Chem. Soc. **80**, 1021 (1958); R. F. Michielli and P. J. Elving, J. Am. Chem. Soc. **90**, 1991 (1968); see also A. J. Fry, "Synthetic Organic Electrochemistry", Harper & Row, New York, 1972, p. 208.

³ W. J. M. van Tilborg and C. J. Smit, Tetrahedron Lett. **1977**, 3651.

⁴ W. J. M. van Tilborg and C. J. Smit, Recl. Trav. Chim. Pays-Bas, **97**, 89 (1978).

⁵ A. Bewick and H. P. Cleghorn, J. Chem. Soc., Perkin II, **1973**, 1410 and A. Bewick and D. J. Brown, J. Chem. Soc. Perkin II, **1977**, 99.

⁶ D. Brown and L. Horner, Justus Liebigs Ann. Chem. **1977**, 77.

⁷ C. K. Mann and K. K. Barnes, "Electrochemical Reaction in Non-aqueous Systems", M. Dekker Inc., New York, 1970, p. 452.

of acetophenone, lithium fluoride – unlike lithium chloride and lithium perchlorate – did not give any reductive wave up to -3.0 V (Fig. 2, curve a). Apparently, the relatively strong covalent character of the lithium-fluoride bond hampers the electron transfer to a sufficiently large extent to prevent lithium amalgam formation. The most remarkable result to emerge from our attempts to reduce acetophenone in these media was the finding that *acetophenone cannot be cathodically reduced in dry acetonitrile with lithium fluoride as the conducting salt* (Fig. 2, curve b).

Addition of even a trace amount of tetraethylammonium fluoride (TEAF) to this electrolyte mixture evokes the intense acetophenone reduction waves mentioned in Table I and Fig. 1 (Fig. 2, curves d and e). Whether or not tetraalkylammonium salts play a similar role in the reduction of acetophenone in the presence of LiCl or LiClO₄ as the conducting salts is not known because any reduction wave of acetophenone would be obscured by the intense lithium reduction waves.

Lithium amalgam formation, however, is prevented by addition of a molar excess of tetraethylammonium fluoride (TEAF) to LiClO₄ or LiCl solutions. Clearly, owing to their "hard" character, the fluoride anions of TEAF are effectively transferred to the "hard" lithium ion (Table II).

Polargraphic behaviour of acetophenone

In order to gain a better insight into the peculiar role played by the tetraethylammonium salts in the reduction of acetophenone, we have studied its reduction in more detail (Table III). As reported previously¹ the electro-reduction of acetophenone in aqueous medium whether in the presence or absence of tetraethylammonium ions is a diffusion-limited process. In the aprotic solvent acetonitrile we found this electro-reduction to be adsorption controlled at low concentrations of tetraethylammonium conducting salts. This follows from the existence of a linear relationship between limiting current and the mercury column height (Fig. 3b). In spite of the adsorption control, the limiting current proved to be linearly dependent on the acetophenone concentration in the lower concentration region ($< 5 \times 10^{-3}$ mol/l; Fig. 4). These findings are explained by assuming that the adsorption follows a Langmuir adsorption⁸ isotherm. This explanation is in accord with the work of Behr⁹, who showed that the adsorption of heptanone on mercury follows a Langmuir isotherm in solvents of moderate and low polarity.

⁸ B. B. Damaskin, D. A. Petrii and V. V. Batrakov, "Adsorption of Organic Compounds on Electrodes", Plenum Press, New York, 1971, p. 86.

⁹ B. Behr and M. Drogowska, J. Electroanal. Chem. **82**, 317 (1977).

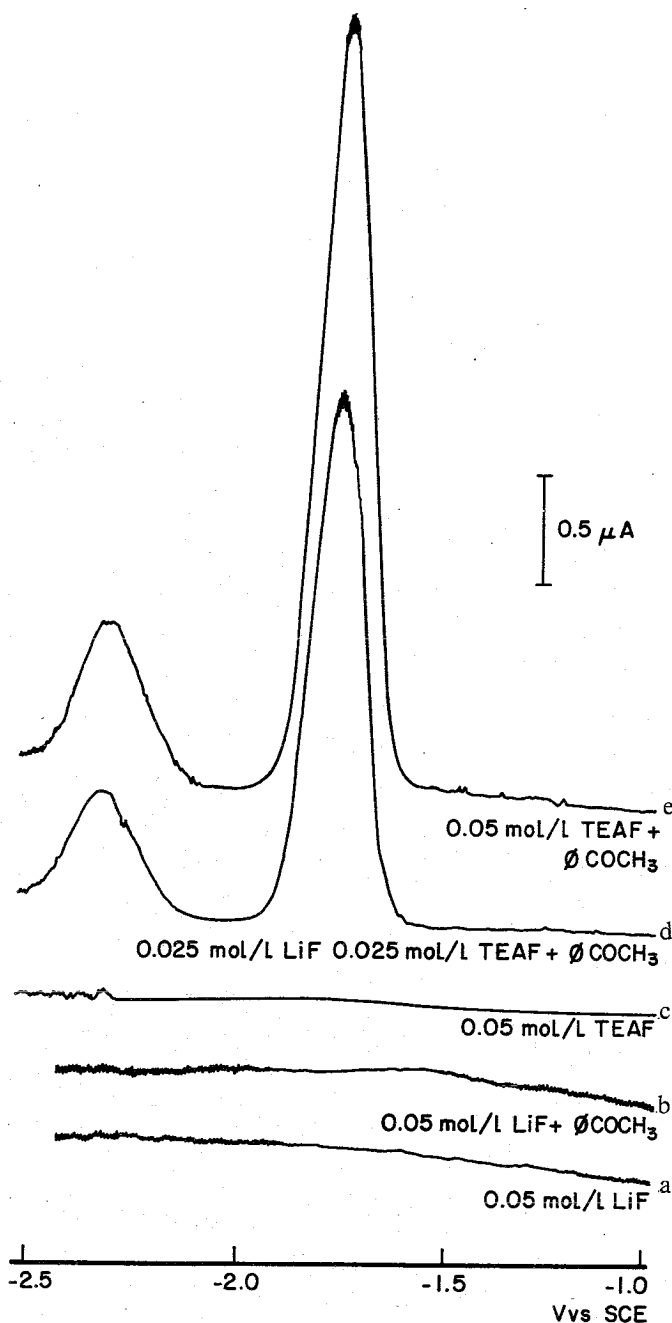


Fig. 2. Catalysis of the electro-reduction (AC 300 Hz, 5 mV) of acetophenone by tetraalkylammonium salts (the two lower traces were recorded at a $100 \times$ higher sensitivity).

Table III Current-limiting factors in the polarographic reduction of acetophenone

Solvent	Conducting salts (mol/l)	Ketone (mol/l)	$E_{1/2}$ (V vs SCE)	$-I_{lim}$ (μ A)	Current-limiting factor	I_d^a	αn^b	n^c
CH ₃ CN	TEAClO ₄ (0.05)	acetophenone (8.40×10^{-3})	-2.00	26.4	adsorption	—	—	—
CH ₃ CN	TBAClO ₄ (0.05)	"	-1.99	29.1	adsorption	—	—	—
CH ₃ CN	TEAClO ₄ (0.8)	"	-1.96	21.7	diffusion	2.75	0.91	0.76
CH ₃ CN	TEAClO ₄ (0.05)	<i>p</i> - <i>n</i> -butyl-acetophenone (5.9×10^{-3})	-2.06	15.4	adsorption	—	—	—
CH ₃ CN	TBAClO ₄ (0.05)	"	-2.06	16.3	diffusion	2.81	0.96	1.04
H ₂ O	KF(0.5)	acetophenone (7.72×10^{-3})	-1.56	19.5	diffusion	2.40	0.78	1.00
H ₂ O	KF(0.5)/TEAF(5.10^{-5})	"	-1.56	23.3	diffusion	3.11	0.90	1.30

^a diffusion current constant.

^b determined according to Tomes' criterion¹⁴ for irreversible processes applied to an extended scale polarogram.

^c computed from the Ilcovic equation with $D(\text{H}_2\text{O}) = 1.10 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$ or $D(\text{CH}_3\text{CN}) = 2.6 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$ as the diffusion constant of the acetophenones, based on comparison with related compounds¹¹.

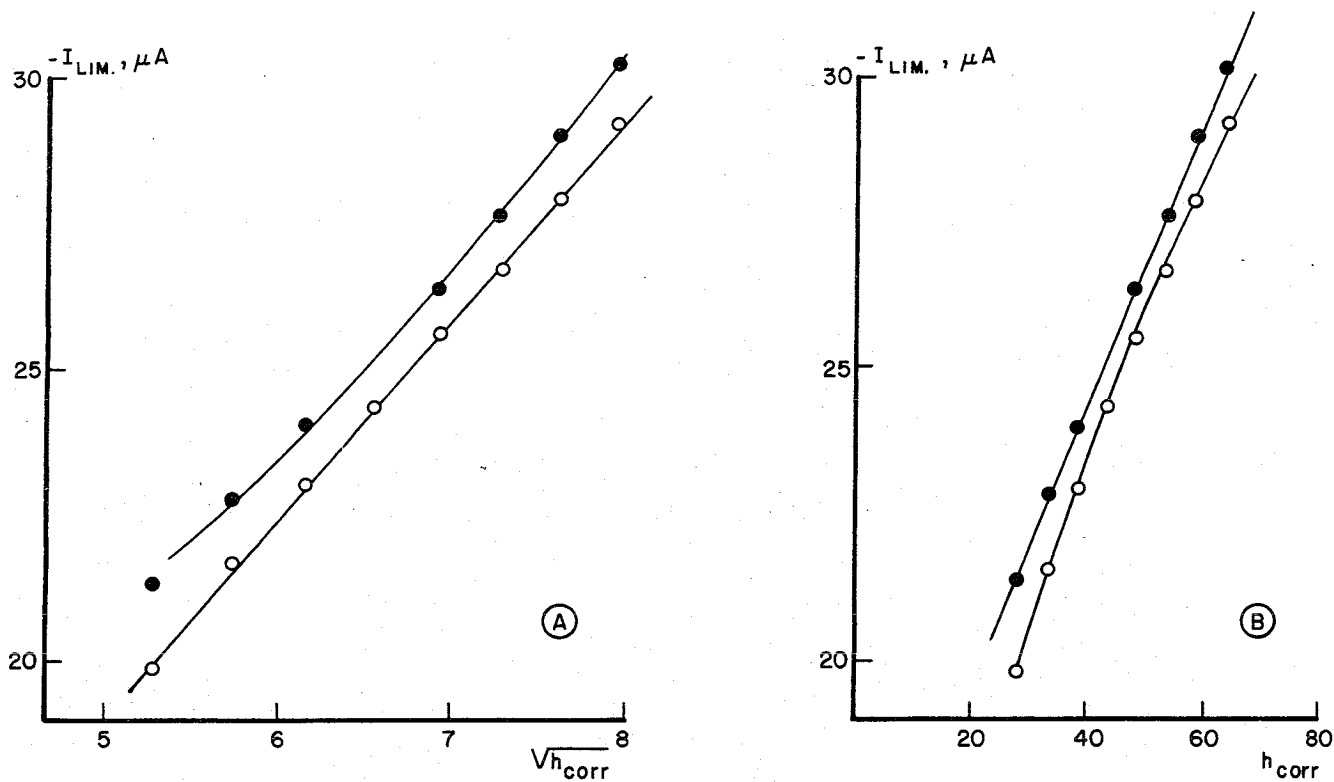


Fig. 3. Plots of limiting polarographic current vs square root of the mercury column height (A) and vs the mercury column height (B) for acetophenone ($5 \cdot 10^{-3}$, mol/l first wave) reduction at low (● 0.05 mol/l) and high (○ 0.8 mol/l) TEAP concentration.

At high conducting salt concentrations (0.8 mol/l TEAP) the reduction becomes diffusion limited (limiting current linearly related to the square root of the mercury column height, Fig. 3a). Apparently, the increased coverage of the electrode surface by ammonium ions results in a displacement of the carbonyl compound. At high ammonium ion concentrations the situation in acetonitrile resembles that in water where the reduction is also diffusion controlled and where, at the potential of the reduction, the electrode surface is also covered with a layer of tetraalkylammonium ions.

The effect observed upon increasing the concentration of the conducting salt can also be brought about by replacing the tetraethylammonium salt by the more strongly adsorbing tetrabutylammonium salt. The latter salt, at low concentrations, was unable to displace acetophenone, but in contrast to tetraethylammonium salts, it proved capable of displacing *p-n*-butylacetophenone (Table III).

The first waves of the electro-reductions in acetonitrile discussed so far are concluded to be one-electron transfers: (a) Two distinct DC polarographic waves of comparable height (Fig. 1) are observed for the reduction of acetophenone, which points to the occurrence of two successive one-electron transfers.

(b) Electrolysis on a preparative scale at the potential of the first reduction wave exclusively produces acetophenone pinacol³, the direct product of a one-electron reduction.

(c) Estimations of "n" based on the Ilcovic equation (in the case of diffusion control) all lead to values of "n" (see Table III) that are compatible only with a one-electron transfer.

This conclusion leads to values for the electron transfer coefficient of ca. 0.9, substantially deviating from the common value¹⁰ of 0.5. Such a high value for α suggests a rather asymmetric activation energy profile for the electron transfer, the transition state being situated at an unusually large distance from the electrode surface¹¹. In our opinion this phenomenon lends additional support to what has been proposed for the reduction in water where the carbonyl compounds are thought to be reduced on top of an ammonium adsorbate layer. In agreement with this we find in water a higher value for α when tetraethylammonium salts

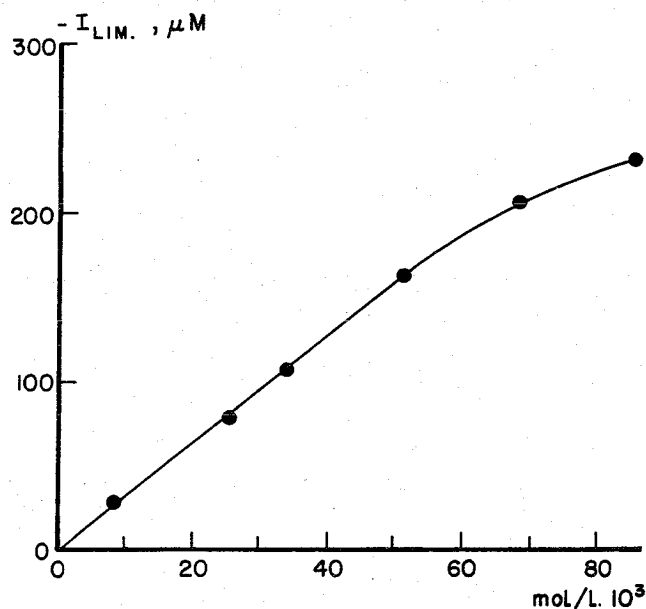


Fig. 4. Relation between limiting current and acetophenone concentration in the polarographic reduction of acetophenone in acetonitrile in the presence of 0.05 mol/l TEAP.

are present than when KF is used as the conducting salt (Table III).

Mechanism of acetophenone reduction

The main factor generally recognized to govern the electron transfer in an electro-chemical process is the very high electric field strength¹² in the double layer, which is of the

¹⁰ J. P. Brenet and K. Traore, "Transfer Coefficients in Electrochemical Kinetics", Academic Press, London, 1971, p. 152.

¹¹ J. O'M. Bockris and A. K. N. Reddy, "Modern Electro-chemistry", Vol. II, Plenum Press, New York, 1970, p. 922.

¹² J. O'M. Bockris and D. M. Dražič, "Electro-chemical Science", Taylor and Francis Ltd, London, 1972, p. 26.

order of 10^9 V m^{-1} . Our work shows that even for a well polarizable bond such as the carbonyl bond, this field strength is insufficient to facilitate electron transfer in an aprotic medium. In a protic environment, however, such a reduction does occur. This is explained² by assuming that the polarization of the carbonyl bond, because of the strong electric field, increases its basicity. Subsequent protonation, or hydrogen bond formation, further enhances the polarization of the carbonyl double bond, and as a result facilitates the electron transfer². Our observation that in an aprotic environment the tetraalkylammonium ion can mimic the role of the proton is peculiar since no covalent bonding can exist between the carbonyl oxygen and tetravalent nitrogen. We believe that the effect of the ammonium ion (proton) can be rationalised as follows:

In a cathodic process electrons are transferred from the negatively charged electrode to the lowest unoccupied molecular orbital (LUMO) of the acceptor molecule. From frontier orbital theory¹³ we can conclude that this process will be governed by two parameters: the energy level of the LUMO and the value of the LUMO coefficients. Both of these will be influenced by an approaching positive (cation) charge. In order to arrive at a qualitative picture, we have carried out simple Hückel MO calculations on four acetophenone π -electron systems:

- (1) the unperturbed molecule,
- (2) acetophenone with a unit positive charge located at 0.3 nm from the carbonyl oxygen atom on the extended C—O σ bond axis,
- (3) acetophenone with a positive charge located at a distance of 0.2 nm from the carbonyl oxygen, and
- (4) acetophenone with a positive charge at 0.1 nm distance from the carbonyl oxygen.

These distances were chosen because CPK molecular models show that the minimum distance between a tetraalkylammonium ion and carbonyl oxygen is about 0.3 nm, since 0.1 nm is the OH bond length (effective protonation) and since a distance of 0.2 nm was thought to resemble the bond length in an oxygen-hydrogen bridge. The results of these calculations, represented in Fig. 5, indicate the following:

(a) An approaching positive charge induces an energy decrease of the molecular orbitals. The LUMO, which is of special relevance to our case, decreases by about 3 eV relative to unperturbed acetophenone when a positive charge (ammonium ion) is brought at a distance of 0.3 nm from the carbonyl oxygen atom. An approach up to ~ 0.2 nm distance (hydrogen bridge) causes another 1 eV decrease in LUMO energy. Although Hückel calculations give an overestimation of these effects, the results are in line with our observations, the reduction potentials in water being -1.5 V , in acetonitrile containing tetraethylammonium fluoride $-1.76/-2.30 \text{ V}$ and in acetonitrile/lithium fluoride $< -3.00 \text{ V}$.

(b) The electron transferred in the electrochemical step is partially localized on the carbonyl carbon atom. The LUMO coefficients calculated indicate a substantial delocalization into the aromatic nucleus. This aromatic delocalization increases – at the cost of the localization on oxygen – when the distance between the oxygen and the positive charge decreases. As can be seen from the charge distribution on the non-reduced “protonated” molecule, the oxygen atom bears almost two electrons and thus there is virtually no room for delocalizing an additional unpaired electron.

The unpaired electron density on the carbonyl carbon atom is maximal (ca. 50%) when the positive charge is located at a distance of about 0.2 nm from the carbonyl oxygen atom. This situation seems to be optimal for pinacol formation.

On the basis of our observations, supported by the aforementioned Hückel calculations, we conclude that the catalytic effect of tetraalkylammonium ions is exerted* in a type of “collision-determined complex”. In this context the observed dependence of the reduction potential on the nature of the anion of the conducting salt (Table I) can be explained

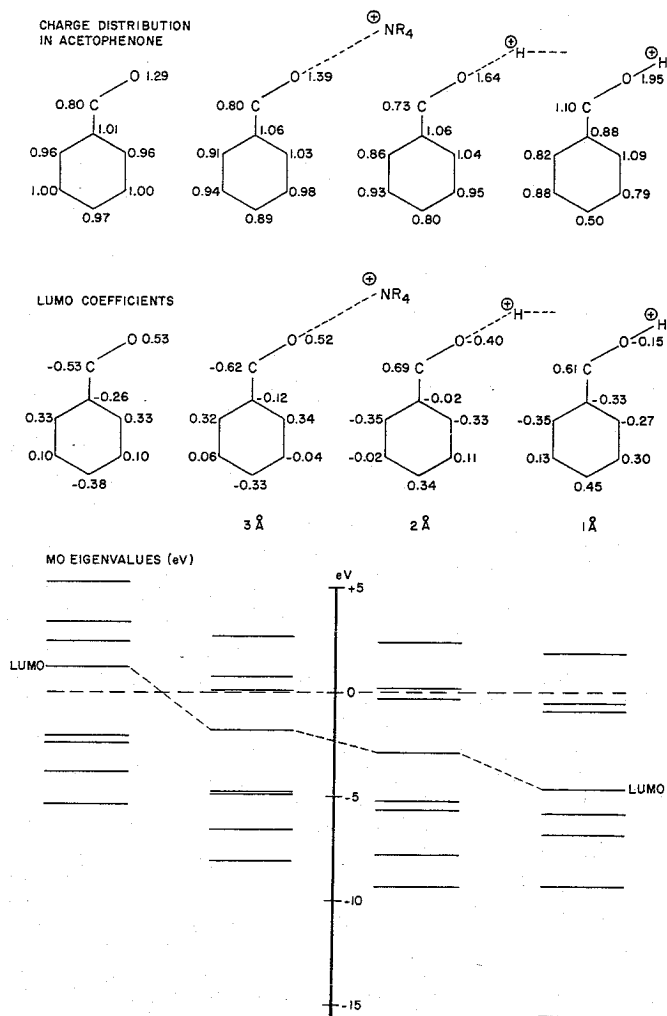


Fig. 5. Effect of a unit positive charge on the reduction potential of acetophenone as derived from Hückel calculations. Assumptions: potential difference between carbon and oxygen = $\beta/2$ (-1.25 eV). Potential at carbon is set at 0 eV , which only affects the absolute scale. C—O bond length 0.122 nm , C—C bond length 0.140 nm . The effect of an approaching positive charge was calculated on the basis of the effect of the charge in electrostatic potential at each atom of the molecule caused by such a charge situated at a distance of 0.1, 0.2 and 0.3 nm from the oxygen atom on the C—O bond axis of acetophenone.

in terms of availability of positive charge. The extremely basic/nucleophilic fluoride ion will, even in a solvent with a rather low acceptor number¹⁴ such as acetonitrile, be solvated by a shell of solvent molecules. Consequently, the tetraalkylammonium fluoride will form completely solvent separated ion pairs in acetonitrile, whereas a solution of e.g. tetraalkylammonium perchlorate will contain intimate ion pairs. In the latter case, part of the positive charge of the ammonium ion will be compensated by the negative charge of the adjacent anion, the effect on the electrostatic potential will decrease and as a result the reduction potential will increase.

* We do not believe that longer-living complexes between the carbonyl compound and ammonium ions exist, since infrared measurements of acetophenone in acetonitrile in the presence of comparable amounts of the conducting salts mentioned in Table I, do not reveal a shift in infrared carbonyl frequency exceeding the error of the measurements ($\pm 1 \text{ cm}^{-1}$).

¹³ I. Fleming, “Frontier Orbitals and Organic Chemical Reactions”, J. Wiley & Sons, London, 1976.

¹⁴ V. Gutman, *Coord. Chem. Rev.* **18**, 225 (1976), and references cited therein.

Table IV Effect of tetraethylammonium perchlorate concentration on mercury dropping time, limiting current and reduction potential in the polarographic reduction of acetophenone (5.10^{-3} mol/l)

TEAP (mol/l)	Dropping time (s)	Limiting current ($-\mu\text{A}$)	Limiting current ^a ($-\mu\text{A}$)	Reduction potential (V vs SCE)
0.05	2.7	28.1	20.3	-2.02
0.10	1.7	28.0	22.8	-2.02
0.20	1.9	28.0	23.0	-2.00
0.40	2.7	26.4	22.6	-1.96
0.80	3.1	25.0	19.6	-1.94

^a Limiting current at an imposed (hammer mechanism) dropping time of one second.

Our hypothesis that the carbonyl bond is activated upon collision with positively charged ammonium ions suggests that the limiting current should depend on the ammonium ion concentration. This was found not to be the case (Table IV). It should be realized, however, that an increase of the ammonium ion concentration has two opposite effects: on the one hand, it will, no doubt, increase its concentration in the adsorbate layer (as reflected in the observed changes in dropping time), but on the other, it will decrease the concentration of acetophenone in the adsorbate layer. The fact that up to an ammonium ion concentration of ca. 0.2 mol/l the limiting current slightly increases (imposed dropping time and therefore almost constant drop size) suggests that up to this concentration the effect of increased ammonium ion concentration in the adsorbate layer dominates. Beyond that concentration, adsorbed acetophenone is increasingly being displaced* and the limiting current drops.

Conclusions

- (1) In an aprotic medium (acetonitrile), carbonyl compounds such as acetophenone cannot be reduced in the presence of lithium fluoride as the conducting salt.
- (2) Tetraalkylammonium ions strongly catalyse the electro-reduction of carbonyl compounds in an aprotic environment.
- (3) The catalysis by tetraalkylammonium ion is due to an increased polarization of the carbonyl double bond in a collision-determined complex. Of course, the high field strength operative in the double layer assists the reduction by its polarizing power, but this assistance itself is insufficient to make electron transfer possible.
- (4) The electro-reduction of carbonyl compounds in aprotic media is further governed by adsorption processes of both the carbonyl compound and the ammonium ions. The fact that these two processes obey different adsorption isotherms causes a complete displacement of the carbonyl species from

the double layer at high ammonium ion concentrations. In such cases the catalytic effect of the ammonium ions can decrease.

(5) At high ammonium ion concentrations in an aprotic environment, the process of the electro-reduction of acetophenone can be described in terms of a reduction on top of a tetraalkylammonium ions adsorbate layer, as was found¹ to be the case in aqueous medium.

(6) The nature of the anion (soft/hard¹⁶) of the tetraalkylammonium conducting salt directly affects its solvation and the electrostatic field induced by the positive charge of the ammonium ion. This results in a change in the reduction potential of the carbonyl species in the sense that less solvated anions induce a cathodic shift.

Experimental

Acetonitrile (Merck, Uvasol) was purified and dried prior to each experiment by percolation over a 30 cm column of dry (Brockman V) neutral alumina. Acetophenone and *p*-*n*-butylacetophenone were commercially available and used without further purification. All the conducting salts were dried for at least 48 h over P_2O_5 in vacuum (1 Pa) at 60°C. The removal of the last traces of water from TEACl proved to be extremely difficult: drying for one week at 100°C was needed. Solutions were prepared in a glove box under helium and were kept under argon in the polarographic cell. To remove residual traces of oxygen, the solution was purged for at least 10 min with argon prior to recording the polarogram.

Polarograms were recorded on a Tacussel polarograph, type PRG 3. Recording conditions: scan speed (scale): 1.25 mVs⁻¹ (100 mVcm⁻¹); for extended scale polarograms: 0.25 mVs⁻¹ (20 mVcm⁻¹). AC polarograms: AC amplitude: 5 mV; AC frequency: 300 Hz. Reduction potentials and the values for αn were always obtained via an extended scale polarogram. The value of αn was calculated using Tomes criterion¹⁷ for irreversible electron transfer: $\alpha n = 51.7/(E_4 - E_2)$.

Cyclic voltammetry was carried out using a PAR type 173 potentiostat, a PAR type 175 universal programmer and a Hewlett Packard type 7045 X-Y recorder or a Tektronix type 5103 N X-Y oscilloscope.

* In fact we are dealing with a competition between two adsorption processes, one (acetophenone) being governed by a Henry type isotherm, the other (ammonium ions) by the Frumkin isotherm. At low concentrations of ammonium ions (Frumkin) the species following the Henry isotherm (acetophenone) is favoured whereas at higher ammonium ion concentrations the Frumkin isotherm dominates¹⁵.

¹⁵ cf. ref. 8, p. 90, Fig. 17.

¹⁶ G. Klopman, J. Am. Chem. Soc. **90**, 223 (1968).

See also R. G. Pearson, J. Am. Chem. Soc. **85**, 3533 (1963) and R. G. Pearson and J. Songstad, J. Am. Chem. Soc. **89**, 1827 (1967).

¹⁷ A. J. Fry, "Synthetic Organic Electrochemistry", Harper & Row, New York, 1972, p. 74.