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Temperature Effects on Electrode Processes. IV. The Effect of Angular Constraints on the Entropy of Formation of Anion Radicals of Compounds Related to Benzophenone

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The entropy of the formation of the anion radicals of compounds related to benzophenone was observed to be dependent upon the charge delocalization as reflected by the planarity of the ions. This is demonstrated by the decreasing trend in the entropies as the angles between the aromatic rings and the carbonyl groups increase due to steric restraints in the series 9-fluorenone (−9.8 cal/K mol), 9-anthrone (−10.1 cal/K mol), benzophenone (−12.8 cal/K mol) and 2,6-dimethylbenzophenone (−14.6 cal/K mol). The dependence of the entropy of formation of the anion radicals of benzophenones bearing methyl substituents on structure was observed to be complex and to arise from both steric and electronic effects. The entropies were observed to correlate reasonably well with the angular relationship of the carbonyl group to the benzene rings. It is pointed out that solvation of both the anion radicals and of the neutral ketones must be taken into account in analyzing the entropies of formation of the anion radicals.

Previous papers in this series have established that the entropy changes of reversible electrode processes are highly sensitive parameters depending upon the degree of reorganization of the environment around a species on which the charge is changing.[1-3] Entropy changes ranging from −0.9 cal/K mol for the formation of the highly symmetrical anion radical of triphenylene[1] to 25.3 cal/K mol for the formation of the charge localized cation radical of thianthrene have been evaluated.[2] The recent work[1-3] has invalidated the conclusions, based on limited data,[4,5] that the temperature coefficients of reversible redox potentials of aromatic compounds in aprotic solvents are of the order of 0.4 mV/K which corresponds to about 10 cal/K mol.

The previous paper in this series demonstrated that the contributions of polar and steric effects during the reduction of alkyl substituted nitrobenzenes could be evaluated. The polar effect was found to be mainly manifested in the properties of the neutral molecules while the steric effect exerted the greatest influence on the anion radicals.[3]

Benzophenones and related molecules which are reduced reversibly in proton donor poor solvents offer a further testing ground for the entropy effects in reversible electrode processes. Benzophenone is reduced reversibly to the anion radical in aprotic solvents and in the absence of proton donors the anion radical can be reduced reversibly as well.[6] Halobenzophenone reduction and the subsequent cleavage of the corresponding anion radicals have been studied intensively[6-11] as has reduction of the related compound 9-fluorenone.[12] Both polar and steric effects upon the reversible reduction potentials of methyl substituted benzophenones have recently been studied and compared to the interplanar angles between the phenyl rings and the carbonyl group.[13]

As illustrated in structures *1* to *7*, the average angles between the planes of the two phenyl rings and that of the carbonyl group of benzophenone and methyl substituted benzophenones depend upon the steric interactions of the groups in the 2,6- and 2′,6′-positions. In the structures *1* to *7*, presented by Rekker and Nauta,[14] the circles designate volumes occupied by methyl groups. Even in benzophenone,

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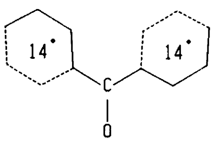

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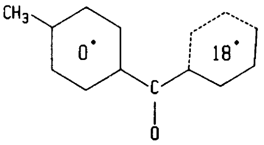

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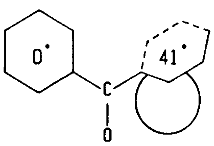

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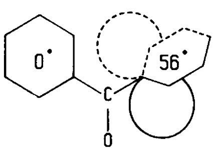

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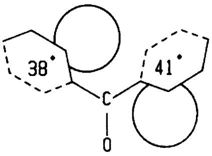

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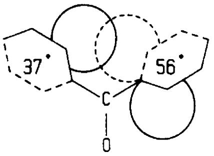

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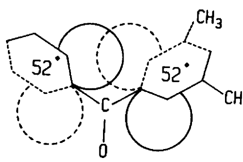

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the two phenyl rings cannot be coplanar with the carbonyl group at the same time and structure *1* gives the favored conformation. Successive substitutions with methyl groups bring about increasing deviations from planarity as shown in structures *3* to *7*. The angles shown were calculated from oscillator strengths (f) obtained from absorption spectra.[14] Estimates of the interplanar angles have also been made by ^{1}H NMR [15] and ^{13}C NMR [16] spectroscopy.

The thermodynamic parameters for a reversible electrode process identified in eqn. (1) are a

$$-E^{\text{rev}} = (\Delta H - T\Delta S)/nF \qquad (1)$$

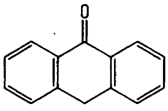
reflection of the energy differences between the neutral and charged species in solution in reaction (2). Thus, the features of importance in the present context are not the conformations of the molecules undergoing charge transfer but rather the differences in conformations between the neutral and charged species. For example, if the favored conformation of benzophenone is *1* and this is also the favored conformation of the anion radical and the same relationship would hold for the substituted compounds and anion radicals, there would be no influence of conformation or ΔH for the reduction. There could still be an effect on ΔS since the solvation of the anion radicals and the neutral molecules differ appreciably. Since the energy of an electronic absorption band gives the difference in energy between an occupied and unoccupied orbital, usually the lowest energy one, in the ground state good correlations are usually obtained between transition energies and electron affinities or ionization potentials.[17] Thus, electrode potentials often correlate with transition energies as well. As we pointed out earlier,[2] there is no fundamental reason why such correlations should exist since the related parameter is ΔH rather than E^{rev}. Data reported for highly substituted nitrobenzenes suggested that steric hindrance to solvation of the anion radicals can give rise to unexpected entropy changes.[3] Structures *4* to *7* for the methyl substituted benzophenones suggest that the reduction of these compounds might provide further insight into the question posed above.

$$\text{Molecule} \pm e^- \rightleftarrows (\text{Ion radical})^{\mp} \qquad (2)$$

In this paper we report the results of measurements of the temperature coefficients of the reversible reduction potentials for benzophenone, methyl substituted benzophenones, 9-anthrone and 9-fluorenone in acetonitrile.

RESULTS AND DISCUSSION

The reversible potentials and the temperature coefficients for the reduction of compounds *1* to *13* are gathered in Tables 1–3. All dE^{rev}/dT refer to measurements in acetonitrile over about 40 K using phase selective second harmonic *a.c.* voltammetry. As in the previous paper,[3] raw data are not reported but typical data for similar measurements have been presented in other papers.[1,2] The precision in the electrode potential measurements was as before of the order of ± 0.2 mV which gives rise to an error in dE^{rev}/dT of the order of ± 0.01 mV/K or ± 0.2 cal/K mol in ΔS. Details of the measurements and data precision were discussed earlier.[1]



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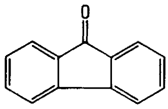

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The degree of coplanarity of the phenyl rings and the carbonyl group increases in going down the series, *1* to *11* to *12*. Since we expect the entropy change to be dependent primarily upon the charge distributions in the resulting anion radicals, any change in geometry resulting in decreased overlap of the carbonyl pi system with those of the phenyl rings is expected to bring about a larger entropy decrease upon charge transfer. Thus, our prediction, based on prior experiences,[1-3] is that the entropy change will become less negative in going from *1* to *11* to *12*. This expectation is fulfilled by the order shown in Table 1. The enthalpy changes, relative to that for the reduction of *12* show no systematic trend.

The thermodynamic parameters for the reduction of unsymmetrically substituted benzophenones are given in Table 2. A slightly lower entropy decrease than for the parent benzophenone was observed during reduction of the 4-methyl substituted isomer *2*. Since substituents in the 4,4′-positions cannot exert a steric effect, this small difference must be a consequence of the polar effect of a methyl group conjugated with the carbonyl group. A 2-methyl substituent (*3*) brought about a greater entropy decrease and that for 2,6-dimethylbenzophenone (*4*) was still greater. Thus, as expected, the steric effect predominates for substituents in the 2,2′-positions. The polar effect of the 4′-methyl substituent in (*10*) resulted in an entropy decrease during reduction intermediate between those for *3* and *4*. The trend observed with *ortho* methyl groups bringing about a larger entropy decrease does not continue with the inclusion of still more substituents. The inclusion of the third *ortho* substituent in *6* was actually accompanied by a lowering in the entropy decrease, as compared to *4*, to a value less than that for benzophenone. Thus, the crowded structures do not fit in the same trend as that observed with the lesser substituted compounds.

It is evident from the values of the thermodynamic parameters for the reduction of benzophenones symmetrically substituted with

Table 1. Entropy and relative enthalpy changes for the formation of anion radicals of aromatic ketones in acetonitrile.

No.	Name	$(-\mathrm{d}E^{\mathrm{rev}}/\mathrm{d}T)$/ mV K^{-1}	$-E^{\mathrm{rev}}_{273.2}$/ mV^{a}	$-\Delta S_{273.2}$/ cal K^{-1} mol^{-1}	$\Delta\Delta H$/ kcal mol^{-1} ^{b}
1	Benzophenone	0.557	1967	12.8	9.29
11	9-Anthrone	0.436	1942	10.1	9.45
12	9-Fluorenone	0.426	1529	9.82	0

[a] Measurements at a mercury electrode *vs.* Ag/Ag$^+$(CH$_3$CN). [b] Calculated from the reversible potentials and entropy changes relative to that for 9-fluorenone.

Table 2. Entropy and relative enthalpy changes for the formation of anion radicals of unsymmetrically substituted benzophenones in acetonitrile.

No.	Substituents	$(-\mathrm{d}E^{\mathrm{rev}}/\mathrm{d}T)$/ mV K^{-1}	$-E^{\mathrm{rev}}_{273.2}$/ mV^{a}	$-\Delta S_{273.2}$/ cal K^{-1} mol^{-1}	$\Delta\Delta H$/ kcal mol^{-1}
1	None	0.557	1967	12.8	9.29
2	4-Methyl	0.538	1976	12.4	9.60
3	2-Methyl	0.569	2004	13.1	10.1
10	2,4′,6-Trimethyl	0.574	2078	13.2	11.7
4	2,6-Dimethyl	0.633	2018	14.6	9.97
6	2,2′,6-Trimethyl	0.537	2104	12.4	12.6

[a] Measurements at a mercury electrode *vs.* Ag/Ag$^+$(CH$_3$CN).

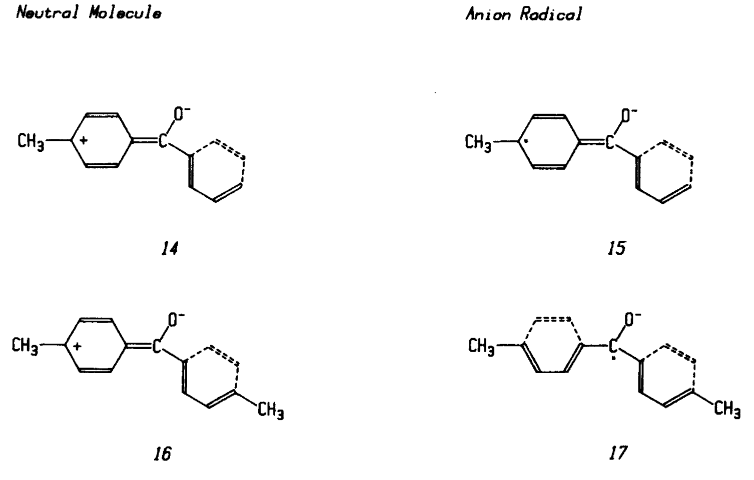
Table 3. Entropy and relative enthalpy changes for the formation of anion radicals of symmetrically substituted benzophenones.

No.	Substituents	$(-\mathrm{d}E^{\mathrm{rev}}/\mathrm{d}T)$/ mV K^{-1}	$-E^{\mathrm{rev}}_{273.2}$/ mV[a]	$-\Delta S_{273.2}$/ cal K^{-1} mol^{-1}	$\Delta\Delta H$/ kcal mol^{-1}
13	4,4′-Dimethyl	0.468	2066	10.8	12.1
1	None	0.557	1967	12.8	9.29
8	2,2′,4,4′-Tetramethyl	0.589	2192	13.6	14.3
5	2,2′-Dimethyl	0.630	2149	14.5	13.0
9	2,2′,4,4′,6,6′-Hexamethyl	0.367	2366	8.46	19.7

[a] Measurements at a mercury electrode *vs.* $Ag/Ag^+(CH_3CN)$.

methyl groups listed in Table 3 that the effects are not additive. For example, the entropy decrease observed during the reduction of 4,4′-dimethylbenzophenone differs from that of the parent by much more than twice the difference observed with 4-methylbenzophenone. This can be rationalized by considering the features of the resonance structures shown in Scheme 1. Methyl substituents could increase the degree of solvation of the neutral molecules as indicated by favoring the charge separation in resonance forms *14* and *16*. The preferred conformation of 4,4′-dimethylbenzophenone is one in which both of the rings are tilted out of the plane of the carbonyl group by 12°, similar to *1*.[14] This indicates that the two methyl groups can participate equally in stabilizing the polarization of the carbonyl group. If we assume that the polar effect of methyl groups is exerted to the greatest extent on the neutral molecule as appears to be the case for the nitrobenzenes,[3] we must allow for a synergistic effect of the two methyls resulting in larger localization of solvent than twice that resulting from a single methyl group. Resonance structures *15* and *17* indicate that the methyl groups do not cause dispersal of the negative charge into the rings. Thus, the results can be explained by larger entropy of solvation of the neutral molecules as compared to benzophenone with little effect on the anion radicals and an overall lowering of the entropy decrease upon formation of the anion radicals.

An empirical equation in which the polar effects of *ortho* and *para* methyl substituents were taken to be the same has been observed to fit entropy data for



Scheme 1.

the reduction of nitrobenzenes in acetonitrile.[3] The added complication of differing spatial relationships of the two phenyl rings relative to the carbonyl group renders the assignment of values to the polar effects of 4-methyl and 2-methyl groups in the benzophenone series somewhat without meaning. The polar effect is surely dependent upon the degree of overlap between the *p* orbital on the carbonyl carbon with the pi systems of the phenyl rings. In fact, an approximately linear relationship has been observed between electrode potentials and a function of the interplanar angles for 4-methyl substituents.[13] The point of importance in the discussion of our data is that the 2,2′-methyl groups surely have a polar effect in addition to the more obvious steric effect. However, the situation is so complicated by the multitude of possible anion radical conformations that there is little hope of being able to separate polar and steric effects on the basis of the limited data available.

We commented earlier on the fact that the reduction of 2,2′,6-trimethylbenzophenone is accompanied by a much smaller decrease in entropy than expected on the basis of a comparison to results from less highly substituted benzophenones. Structure *6* suggests that the crowding caused by the methyl groups could make the solvation shell of the anion radical less ordered than it would be in the absence of the methyl groups. The effect is very much more pronounced during the reduction of 2,2′,4,4′,6,6′-hexamethylbenzophenone (*9*) in which case $\Delta S_{273.2}$ is 4.3 cal/K mol less negative than that observed during the reduction of benzophenone. The environment of the carbonyl group of *9* would be expected to be very similar to that shown for *7* and the carbonyl group is not easily approached by solvent molecules. Thus, the ordering of the solvent takes place around the periphery of the hindered carbonyl group of the anion radical and results in a much smaller entropy decrease than when the solvation is more intimate.

Finally, we can consider the comparison of the entropy changes for the reductions with the oscillator strengths obtained from electronic absorption spectra. The oscillator strengths,[14] like extinction coefficients,[18] give a measure of the degree of conjugation and were used[14] as the parameters to estimate the interplanar angles shown in structures *1* to *7*. We have attempted linear regression correlations of E^{rev}, $\Delta\Delta H$ and ΔS with f. No correlation was observed between f and E^{rev} or $\Delta\Delta H$, the correlation coefficients were 0.26 and 0.11, respectively. On the other hand, ΔS correlates linearly with f with a correlation coefficient of 0.96 and the results can be incorporated into eqn. (3). The

$$f = 0.0550\ (\text{K mol/cal})\ \Delta S + 1.096 \qquad (3)$$

data are summarized in Table 4. The calculated values in the last column are very close to the f values reported.[14] It may well be that the correlation would be even better with more precise measures of f, the difficulties in the estimation of which has been commented on.[16,19]

This study has provided further evidence for the sensitivity of the temperature coefficients of electrode potentials for reversible processes to changes in the solvation processes. In addition, the discussion amply demonstrates that when comparing the thermodynamic parameters of electrode processes to other quantities it is necessary to consider the features of both the

Table 4. The correlation of the entropy changes for the reversible reduction of methyl substituted benzophenones with UV oscillator strengths.[a]

No.	Substituents	$-\Delta S_{273.2}$/cal K^{-1} mol^{-1}	f_{lit}[b]	f_{calc}[c]
1	None	12.8	0.38	0.39
13	4,4′-Dimethyl	10.8	0.50	0.50
8	2,2′,4,4′-Tetramethyl	13.6	0.36	0.35
5	2,2′-Dimethyl	14.5	0.30	0.30
2	4-Methyl	12.4	0.45	0.41
3	2-Methyl	13.1	0.35	0.38
4	2,6-Dimethyl	14.6	0.30	0.29
10	2,4′,6-Trimethyl	13.2	0.36	0.37

[a] UV absorption spectral data from Ref. 14. [b] Oscillator strengths f(tot) for measurements in ethanol listed in Table VIII of Ref. 14. [c] Calculated from linear regression correlation eqn. (3).

charged and neutral species. Neglecting the consideration of one or the other of the partners in the redox couple may lead to serious error. All of the papers in this series have shown that there is a great advantage in separating the electrode potentials into the entropic and enthalpic contributions if a maximum of detail is desired.

EXPERIMENTAL

The experimental procedures and data handling procedures were described in detail in the first paper in this series.[1] Some of the methyl substituted benzophenones were graciously provided by Dr. James Grimshaw in a highly pure state. The other benzophenones as well as 9-fluorenone and 9-anthrone were either commercial samples or were prepared by standard methods and purified by recrystallization before use.

REFBRENCES

1. Svaan, M. and Parker, V. D. *Acta Chem. Scand. B 35* (1981) 559.
2. Svaan, M. and Parker, V. D. *Acta Chem. Scand. B 36* (1982) 351.
3. Svaan, M. and Parker, V. D. *Acta Chem. Scand. B 36* (1982) 357.
4. Hoijtink, G. J. *Recl. Trav. Chim. Pays-Bas 74* (1955) 1525.
5. Van Duyne, R. P. and Reilley, C. N. *Anal. Chem. 44* (1972) 142.
6. Jensen, B. S. and Parker, V. D. *J. Chem. Soc. Chem. Commun.* (1974) 367.
7. Nadjo, L. and Savéant, J. M. *J. Electroanal. Chem. 30* (1971) 41.
8. M'Halla, F., Pinson, J. and Savéant, J. M. *J. Electroanal. Chem. 89* (1978) 347.
9. Savéant, J. M. and Thiébault, A. *J. Electroanal. Chem. 89* (1978) 335.
10. M'Halla, F., Pinson, J. and Savéant, J. M. *J. Am. Chem. Soc. 102* (1980) 4120.
11. Aalstad, B. and Parker, V. D. *Acta Chem. Scand. B 36* (1982) 47.
12. Savéant, J. M. and Tessier, D. *J. Electroanal. Chem. 77* (1977) 225.
13. Grimshaw, J. and Hamilton, R. *J. Electroanal. Chem. 106* (1980) 339.
14. Rekker, R. F. and Nauta, W. Th. *Recl. Trav. Chim. Pays-Bas 80* (1961) 747.
15. Montaudo, G., Finocchiaro, P. and Maravigna, P. *J. Am. Chem. Soc. 93* (1971) 4214.
16. Buchanan, G. W., Montaudo, G. and Finocchiaro, P. *Can. J. Chem. 51* (1973) 1053.
17. Streitwieser, A. *Molecular Orbital Theory for Organic Chemists*, Wiley, New York 1961.
18. Wepster, B. M. *Recl. Trav. Chim. Pays-Bas 76* (1957) 335.
19. Jaffe, H. H. and Orchin, M. *Theory and Applications of Ultra Violet Spectroscopy*, Wiley, New York 1962.

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