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Disproportionation of Dimethyl *p*-Phthalate Anion Radical Paired with Alkali Metal Cation

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This note is concerned with a new example of the disproportionation reaction of the type,[1] $2A^-Na^+ \rightarrow Na^+A^{=}Na^+ + A$ where A^- is a radical anion of an organic substance. According to Hirayama,[2] dialkyl *p*-phthalates when treated with alkali metals, gave the ESR signals characteristic of the radical ion pair A^-Na^+; the intensities however, often decline gradually at room temperature, as a result of some unknown reaction. We have studied the reaction in question spectrophotometrically and have arrived at the conclusion that it is the disproportionation of the above type. The dependence of the reaction upon the alkali metal cation has also been investigated and the result will be discussed in relation to Hirayama's result on the ESR hyperfine structure.

Results and Discussion

When the dimethyl *p*-phthalate (DMT) solution in THF was treated with a metallic mirror of sodium at room temperature, the solution turned purple and gave the ESR signal which was essentially similar to the one reported by Hirayama.[2] Curve 1 in Fig. 1 gives an example of the absorption spectrum of this purple solution. This spectrum was taken as quickly as possible after the appearance of the purple color. When the original concentration of DMT was *ca.* 1×10^{-3}M, the spectrum could be taken with a 1 mm cell. The exact concentration of the purple species (P), however, could not be determined. The spectrum of P-species gradually changed as shown in Fig. 1, with the isosbestic

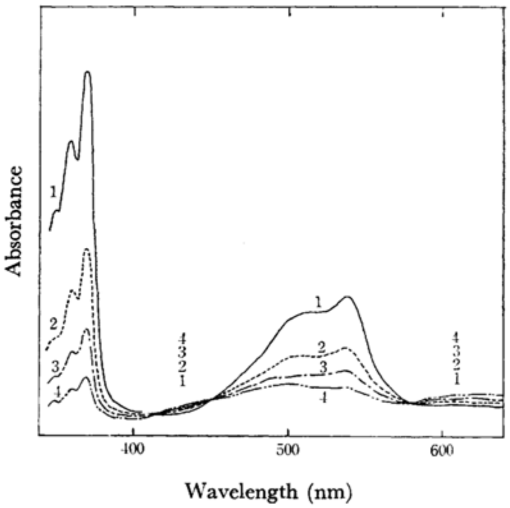

Fig. 1. Change of absorption spectrum in the course of reaction of P-species produced by the treatment with Na.
1, —— 0 sec 2, ----- 5 min 0 sec
3, ——- 19 min 24 sec 4, -·-·- ~40 min

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[1] Somewhat different type of disproportionation has been reported by Evans *et al.*: A. G. Evans, P. B. Roberts and B. J. Tabner, *J. Chem. Soc., B*, **1966**, 269.

[2] M. Hirayama, This Bulletin, **40**, 2234 (1967).

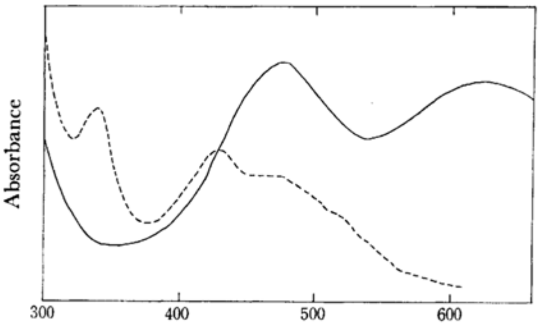


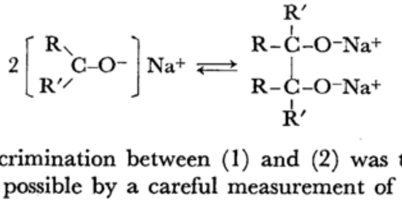
Fig. 2. Absorption spectrum of G-species (——) and that of trinitrobenzene$^-$-Na$^+$ (------) obtained by adding an excess quantity of trinitrobenzene to the G-species solution. The scale of ordinate is different for two curves.

points at 410, 460 and 580 nm. It was established that the reaction is second order in P-species. The resulting solution had a tint of green and gave no ESR signal. This green species (G) is quite stable, living as long as several months, but the exact shape of the spectrum could not be reproduced. The spectrum at the last stage (curve 4), gives the general feature for the G-species. At −80°C the P-species was found to be stable. It was also stable when it was freed from solvent and kept *in vacuo*. Upon introduction of air, the solution of P-species as well as of G-species became light yellow with a white precipitate. The resulting solution from the latter gave the absorption spectrum characterestic for DMT, but the former did not.

In order to examine the radical nature of the G-species, twice as much quantity of trinitrobenzene (TNB) as DMT was added to the green solution. The color at once changed into brown and gave the spectrum of TNB radical anion as shown in Fig. 2. This solution gave the ESR signal similar to the one already reported by Ward.[3] All the above findings strongly support the view that the G-species is either a divalent anion which may be produced by the disproportionation reaction,

$$2\mathrm{DMT^-Na^+} \longrightarrow \mathrm{Na^+DMT^{2-}Na^+} + \mathrm{DMT}, \qquad (1)$$

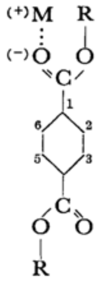
or a dimer of monoanion resulting from dimerization of the following type.[4]



$$2\left[\begin{matrix}\mathrm{R}\diagdown\\ \quad\mathrm{C{-}O^-}\\ \mathrm{R'}\diagup\end{matrix}\right]\mathrm{Na^+} \rightleftarrows \begin{matrix}\mathrm{R'}\\ |\\ \mathrm{R{-}C{-}O^-Na^+}\\ |\\ \mathrm{R{-}C{-}O^-Na^+}\\ |\\ \mathrm{R'}\end{matrix} \qquad (2)$$

Discrimination between (1) and (2) was thought to be possible by a careful measurement of the absorption spectrum, since reaction (1) should recover half as much DMT as DMT$^-$. Although the experiment for this purpose could not be made very accurately, the results were favourable for mechanism (1). As an example, one measurement showed that the increase of the optical density at 242 nm (after a long time) was about one half the decrease at the same wavelength immediately after the treatment with sodium. This is very much larger than the optical density of G species at 242 nm which is 1/5—1/11 of the original DMT.

The Nature of the Radical Ion Paired with Other Alkali Metal Cations. According to Hirayama,[2] the hyperfine structures of ESR for Li and Na are such that the values of $a_{\mathrm{H}}{}^{(2)}$ are larger than $a_{\mathrm{H}}{}^{(3)}$, whereas for K and Cs the values are $a_{\mathrm{H}}{}^{(2)} \approx a_{\mathrm{H}}{}^{(3)}$. He interpreted this as resulting from



the fact that in the former group, metallic ions are located on one of the two carbonyl groups while in the latter group, they are situated in the symmetrical position between the two carbonyl groups. In view of this interpretation, we have examined the absorption spectra and the behaviour of P-species paired with different alkali cations.

The P-species from Li and K gave essentially the same spectra as from Na both in the UV and visible region while the one from Cs showed a clear difference, as shown in Fig. 3 where the free radical anion produced by electrolysis (using tetrabutyl-

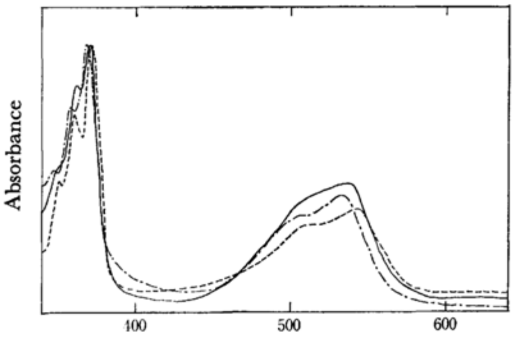


Fig. 3. Absorption spectra of three kinds of P-species, produced by the treatment with Na (------), Cs (——) and by electrolytic reduction (—·—·—): P(Li) and P(K) give essentially the same spectrum as that of P(Na).

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[3] R. L. Ward, *J. Am. Chem. Soc.*, **83**, 1296 (1961).

[4] C. B. Wooster, *ibid.*, **57**, 377 (1957); E. de Bore, *Recuieil*, **84**, 609 (1965).

ammonium perchlorate (T-BAPC) as a supporting electrolyte, [DMT] $\sim 1\times 10^{-3}$M, [T-BAPC] $\sim 1\times 10^{-1}$M) is also shown.

The free radical anion was found to be quite stable at room temperature. The reaction P→G occurred with Li just as with Na, while in the case of K and Cs, the spectrum of P only decayed slowly without the appearance of the G-species.

The present results can, as a whole, be interpreted as the ion pair model presented for the analogous systems. McClelland[5] discussed the ion pair of fluorenon and benzophenone in terms of a point charge model and concluded that the potential minimum lies in the neighbourhood of C=O group. Atherton and Goggins[6] studied the ion pair of pyrazine and reached the conclusion that the potential minimum lies on the two nitrogen atoms for Li and Na, while for K and Cs the potential minimum is above the aromatic ring.

Our result that the reaction P→G occurs for Li and Na but not for K and Cs, is phenomenologically consistent with Hirayama's result, if one assumes that the disproportionation reaction occurs only when the alkali cation is fixed on one of the two carbonyl groups. There is however, one discrepancy in the spectrum of P-species when compared with the ESR structure. Thus the spectrum for K-ion pair is quite the same as for Li- and Na-ion pair, while from ESR, the K-ion pair should behave like Cs. This may be interpreted as follows. The similarity of the electronic spectrum suggests that the above three alkali metal cations are located at a C=O position. On the other hand, Cs^+ ion which is situated above the aromatic ring affects the electronic state in a different way. For K, however, the following situation may exist. The K-ion being larger than Li and Na, its potential minima may be more shallow than those of Li and Na. Then the K^+ ion may be able to move from one carbonyl group to the other. If the transfer frequency is $\gtrapprox 10^7$ sec^{-1}, the two states cannot be separately observed by ESR technique, the resulting hyperfine structure resembling that of Cs^+ ion pair. The absorption spectrum under such circumstances, however, is expected to correspond to one of the two equivalent configurations. If such is the case, the different feature of K^+ in ESR and in UV is very reasonable.

To sum up, the monoradical anion of DMT has tendency to undergo more or less the disproportionation reaction, and the reaction occurs more easily when the alkali cation is located and fixed on one of the two carbonyls.

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[5] B. J. McClelland, *Trans. Faraday Soc.*, **57**, 1458 (1961).

[6] N. M. Atherton and A. E. Goggins, *Trans. Faraday Soc.*, **62**, 1702 (1966); N. M. Atherton, *ibid.*, **62**, 1707 (1966).