

and 3475 Å. with the most intense line at 3050 Å.<sup>8</sup> The remarkable intensity of the emission spectrum indicates unusual stability of the excited species.

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(8) We are indebted to Dr. F. J. Dinan for securing these data.

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### An Unusual Solvent Effect on the Air Oxidation of a Stable Carbanion

Sir:

The rate constants for the air oxidation of the carbanion ( $R^-$ )<sup>1</sup> related to Koelsch's radical ( $R\cdot$ , 2-phenylbis(biphenylene)allyl)<sup>2</sup> vary through a series of aprotic solvents by a factor of at least  $10^5$  (Table I<sup>3</sup>).

**Table I.<sup>3</sup> Solvent Effects on Rates of Anion Oxidation<sup>a</sup>**

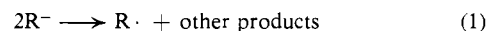
Metal ion	Solvent <sup>b</sup>					
	DMSO, DMF	Pyridine	1,2-DME	THF	2-MeTHF	( <i>n</i> -Bu) <sub>2</sub> O, Et <sub>2</sub> O, Et <sub>3</sub> N, Benzene
Na <sup>+</sup>	$<3 \times 10^{-4c}$		0.34	0.65	$>25^d$	$>25$
K <sup>+</sup>	$<3 \times 10^{-4}$	0.015	0.19	0.63	$\sim 15^e$	$>25$
Cs <sup>+</sup>			0.20	0.61	2.1	

<sup>a</sup> Values tabulated are pseudo-first-order rate constants (sec.<sup>-1</sup>) at 1 atm. of oxygen. Initial concentrations of  $R^-$  were *ca.*  $3 \times 10^{-5} M$  in each case. <sup>b</sup> A rate constant about 0.1 of that found in 1,2-DME was obtained in 12% (by volume) DMF in 1,2-DME. <sup>c</sup> The limiting figure here was estimated on the conservative assumption that a 5% extent of reaction could have been detected, but was not, in a span of 50 hr. It is conceivable that equilibrium considerations may favor reactants in these solvents, but no evidence of lack of complete reaction was found in other solvents. <sup>d</sup> The limit here was calculated from our belief that we could have estimated the rate of any reaction with a half-life greater than about 25 sec., but that these had shorter half-lives at 1 atm. of oxygen. <sup>e</sup> Estimated from two points assuming pseudo-first-order kinetics.

This effect is novel both in the kind of reaction involved and in that more polar solvents *inhibit*, rather than enhance, the rate of a carbanion reaction.<sup>4,5</sup>

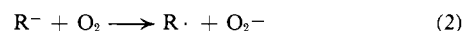
Since the visible spectra of  $R^-$  and  $R\cdot$  contain well-separated bands, both the disappearance of  $R^-$  and the

appearance of  $R\cdot$  could be followed, with the result that good first-order plots (at constant partial pressures of oxygen) gave the same rate constants for each kind of measurement. Equation 1 gives the partial stoichiometry of the reaction in pyridine, 1,2-dimethoxyethane (1,2-DME), tetrahydrofuran (THF), diethyl ether, di-*n*-butyl ether, and 12% *N,N*-dimethylformamide (DMF) in 1,2-DME. For a typical run (1,2-DME; potassium; 1 atm. of oxygen) a plot (eight points, including the



origin) of concentration of  $R\cdot$  produced vs. that of  $R^-$  consumed gives a straight line of slope  $0.50 \pm 0.03$ . It is evident that the reaction is exceptionally clean.

The extensive data of Russell and co-workers, on the base-catalyzed air oxidation of many organic compounds, has been interpreted in terms of reaction sequences in which a one-electron transfer from a carbanion to an oxygen molecule is a key step,<sup>6</sup> one which is presumed to be kinetically isolated in the present study, consistent with over-all second-order kinetics.<sup>7</sup>



The direction of the solvent effect in less polar ethers

and the presence of a distinct metal ion effect in 2-methyltetrahydrofuran suggest that the transition state tends to be more highly aggregated than the reactant ions. In turn, this is consistent with a more concentrated negative charge in the anionic portion of the transition state than in the reactant anion.<sup>8</sup>

At the concentrations employed in these experiments, ionic association appears to be unimportant in THF and 1,2-DME and is presumed to be absent in the more polar solvents pyridine, DMF, and dimethyl sulfoxide (DMSO). It follows that the difference between reactant and transition state anion solvation energies is similar for the two ethers of this group, but that this is not true among all five of these solvents. It is apparent

(1) R. Kuhn and F. A. Neugebauer, *Monatsh.*, **95**, 1 (1964).

(2) C. F. Koelsch, *J. Am. Chem. Soc.*, **79**, 4439 (1957).

(3) Vacuum manifold techniques and manometric devices were used to prepare closed reaction vessels containing reactants at the desired concentrations and pressures. Purified solvents were distilled from storage over sodium benzophenone ketyl (except for DMF and DMSO), ensuring the absence of peroxides. Periodic violent agitation ensured a sustained saturation of the solutions with oxygen, although this was unnecessary, since the solubility of oxygen in all these solvents is probably greater than  $10^{-3} M$  (at 1 atm.: water,  $10^{-3} M$ ; pyridine,  $4 \times 10^{-3} M$ ; diethyl ether,  $5 \times 10^{-3} M$ ; so that initial concentrations of dissolved oxygen constituted a constant excess.

Since in every solvent gaseous oxygen was in equilibrium with the activated complexes, the variations in rate constants reflect *entirely* changes in the activity coefficient ratio  $\gamma_{R^-}/\gamma_{R\cdot}$ , where these activity coefficients are referenced to the fact that the concentrations of  $R^-$  and activated complexes are considered to include all of their ionic aggregates. Where various aggregates are involved, it may be possible later to separate their contributions to the above rates through the dependence of the latter on the initial concentrations of  $R^-$ .

(4) A. J. Parker, *Quart. Rev.* (London), **16**, 163 (1962), has reviewed solvation influences in dipolar aprotic solvents with many references to the rate-enhancing effects of these solvents as compared to protic ones.

(5) (a) D. N. Bhattacharyya, C. L. Lee, J. Smid, and M. Szwarc, *J. Phys. Chem.*, **69**, 612 (1965); (b) D. N. Bhattacharyya, J. Smid, and M. Szwarc, *ibid.*, **69**, 624 (1965). Rate enhancements of carbanion polymerization propagations in more polar ethers are evaluated.

(6) G. A. Russell, with A. J. Moye, E. G. Janzen, E. J. Geels, E. T. Strom, E. R. Talaty, S. Mak, A. G. Bemis, and S. A. Weiner, Preprints, Division of Petroleum Chemistry, 149th National Meeting of the American Chemical Society, Detroit, Mich., April 5-9, 1965, p. A7, and works cited therein, including G. A. Russell, A. J. Moye, and K. Nagpal, *J. Am. Chem. Soc.*, **84**, 4154 (1962).

(7) Variation of the partial pressure of oxygen over 1,2-DME and THF gives pseudo-first-order rate constants which appear to vary linearly with the partial pressure, although a sufficiently wide range of pressures to rigorously exclude a one-half-order pressure dependence of the rates has not yet been examined.

(8) Details of solvation- and aggregation-based arguments of the type which generate these conclusions are given in ref. 4 and 9.

(9) J. F. Garst and E. R. Zabolotny, *J. Am. Chem. Soc.*, **87**, 495 (1965), and earlier papers cited therein.

that direct anion solvation can be important in the more polar aprotic solvents, at least.<sup>4</sup>

While effects of the kind and magnitude found here may not necessarily persist for less stable anions with less delocalized negative charges, it may be that a change to less polar solvents could promote oxidation of some other carbanions which do not seem to oxidize in polar solvents.

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### Enantiomorphism in the Helical Aggregate of Lithium 12-Hydroxystearate

Sir:

It is been known, by electron microscope study, that some crystalline aggregates of soap from lubricating grease consist of fibers in the form of twisted ribbon or helical rope. However, little attention has been paid to the direction of the twist. Hotten and Birdsall<sup>1</sup> pointed out that fibers of lithium 12-hydroxystearate twist by the same hand, but they did not state the direction.

making a copy of the photograph. Therefore, by taking care of these points, we have made electron micrographs of aggregates of lithium 12-hydroxystearate.

12-Hydroxystearic acid (D-form) was purified from a commercial product by recrystallization of its methyl ester from methanol: m.p. 79.3–79.8°,  $[\alpha]^{15D} -0.3 \pm 0.1^\circ$  (pyridine); lit.<sup>4</sup> m.p. 80.5–81°,  $[\alpha]^{19D} -0.41^\circ$  (pyridine). The preparation of lithium soap was virtually identical with that previously described.<sup>1</sup> A highly refined mineral oil having a viscosity of 89.00 centistokes at 37.8° (100°F.), and containing about 69% paraffinic, 24.5% naphthenic, and 6.5% aromatic carbon atoms, was used as the dispersion medium. The specimens for electron microscopy were prepared by the suspension technique.<sup>2c</sup>

The direction of the twist was, as illustrated in Figure 1a, always right-handed, although the form and size of the aggregate were dependent on the experimental conditions. The same result was also obtained with other 12-hydroxystearate soaps (Na, K, Ca, Ba, and Pb soap). On the other hand, the fibers from hydrated mixtures of calcium oleate and calcium stearate exhibit both right-handed and left-handed twists. These results lead us to suggest that the right-handed twist of the aggregates of 12-hydroxystearate soaps may be related to the optical isomerism of this fatty acid, since the commercial sample of the 12-hydroxystearic acid used was the D-form.

In order to confirm this idea, the DL-form and the L-form of 12-hydroxystearic acid were prepared from the

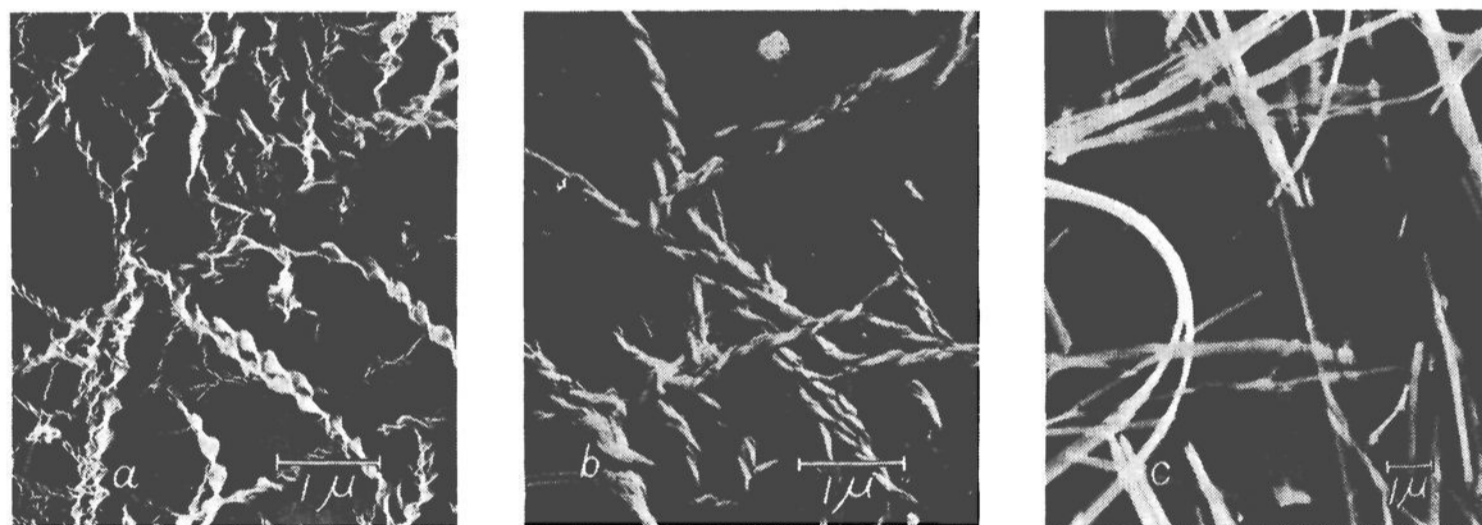


Figure 1. The effect of optical isomerism on the direction of the twist in fibrous aggregates of lithium 12-hydroxystearate: (a) D-form, right-handed twist; (b) L-form, left-handed twist; (c) DL-form, no twist. These photographs were made to show the same direction as that of the twist of the specimen.

On examining the electron micrographs of fibers of lithium 12-hydroxystearate hitherto published, we found that some micrographs<sup>2a-c</sup> exhibit right-handed twist and others,<sup>1,3a,b</sup> left-handed twist. This may be explained by the fact that the direction of the twist of fibers appearing in the photographs is dependent on (1) whether the specimen shadowed previously with metal was exposed directly to the electron beam, or through the support film, and (2) the process of

D-form of this acid. DL-12-Hydroxystearic acid<sup>5</sup> was obtained by reduction of 12-ketostearic acid derived from D-12-hydroxystearic acid. L-12-Hydroxystearic acid was prepared by the Walden inversion of D-12-hydroxystearic acid according to the procedure shown in Figure 2. The aggregates of their lithium soap were examined as described above for the D-form. The results are illustrated in Figures 1b and 1c, which show that the direction of the twist is left-handed for the L-form in contrast with the right-handed twist for the D-form, and that no twisted fibers are obtained for the DL-form. Although the acids of the L-form and DL-

(1) B. W. Hotten and D. H. Birdsall, *J. Colloid Sci.*, **7**, 284 (1952).  
 (2) (a) A. Bondi, *et al.*, *NLGI Spokesman*, **13** (12), 12 (1950); (b) B. W. Hotten, *ibid.*, **19** (1), 14 (1955); (c) G. V. Vinogradov and V. V. Sinitsyn, *J. Inst. Petrol.*, **47**, 357 (1961).  
 (3) (a) M. J. Vold, *et al.*, *NLGI Spokesman*, **18** (5), 8 (1954); (b) A. L. McClellan, *J. Chem. Phys.*, **32**, 1271 (1960).

(4) K. S. Hanssen, *Chem. Ind. (London)*, 1554 (1958).  
 (5) I. Nakajima and S. Toyama, *J. Chem. Soc. Japan*, **81**, 1598 (1960).