

Although it is not possible at this time to provide a complete mechanistic picture for the reactions described, it is clear that they are subject in a major way to minor changes in structure and reaction conditions. These results show that attempts to generalize from isolated experiments such as a stereochemical investigation will in most cases be meaningless, for the stereochemistry of the reaction may change as the reaction progresses. For example, the reaction of diethyl peroxide with optically active phosphine may yield early in the reaction entirely different optical results from those near the end.⁹

(9) R. F. Hudson and M. Green, *Angew. Chem. Intern. Ed. Engl.*, **2**, 11 (1963), have indicated some other problems which are encountered in stereochemical studies with compounds of this type.

(10) National Science Cooperative Graduate Fellow, 1962-1963; Public Health Service Fellow, 1963-1964.

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Proton Transfers in Dipolar Aprotic Solvents. I. Transfers to Fluorenyl and Trityl Anions in Dimethyl Sulfoxide Solution

Sir:

Recently, both Cram¹ and Schriesheim² have presented evidence that proton transfers from *t*-butyl alcohol and other hydroxy compounds to strong hydrocarbon bases in dimethyl sulfoxide (DMSO) solution are diffusion controlled. In this preliminary paper, we report results of competitive proton abstractions from several types of acids by the triphenylmethyl (trityl) and fluorenyl anions in DMSO solution which indicate that diffusion control may be a general characteristic of proton-transfer reactions in such solvents, independent of the nature of the acid and base involved. We suggest a hypothesis which is consistent with the present data and has broad implications as to the general nature of proton-transfer reactions.

Fluorenyl anion in DMSO was produced by adding 1 mmole of fluorene to 2 mmoles of potassium *t*-butoxide in 20 ml. of dry (<60 p.p.m.) degassed DMSO. Trityl anion was produced by adding 1 mmole of triphenylmethane to a solution of 2 mmoles of methylsulfinyl carbanion³ in 25 ml. of DMSO.

The acids were added to these solutions by hypodermic syringe while maintaining rapid stirring by means of a magnetic stirrer. The resulting solutions were poured into 50 ml. of water, extracted with three 20-ml. portions of ether, washed with water, dried with sodium sulfate, and evaporated on a steam bath. The crude products were recrystallized twice from ethanol and analyzed for deuterium by infrared spectrophotometry. The results are reported in Table I.

The data obtained from the addition of D₂O to trityl and fluorenyl anions indicate a rapid exchange of hydrogens of the solvent with deuterium. In fact, 5 min. after mixing, complete equilibration of hydrogen and deuterium throughout the system is

(1) D. J. Cram, *et al.*, *J. Am. Chem. Soc.*, **84**, 4358 (1962), and earlier references cited there.

(2) A. Schriesheim, *et al.*, *ibid.*, **85**, 3002 (1963), and earlier references cited there.

(3) E. J. Corey and M. Chaykofsky, *ibid.*, **84**, 866 (1962).

TABLE I
COMPETITIVE PROTON TRANSFERS IN DIMETHYL
SULFOXIDE SOLUTION

Reacted with	% Fluorene		
	% Fluorene	% 9- <i>d</i> ₁	% 9,9- <i>d</i> ₂
A. Fluorenyl anion			
3.0 ml. of H ₂ O, worked up in D ₂ O	100	0	0
3.0 ml. of D ₂ O, worked up after 1 min.	2	55	43
3.0 ml. of D ₂ O, worked up after 5 min.	59	41	0
9.2 mmoles of nitromethane- <i>d</i> ₃ , worked up after 1 min.	32	58	10
9.2 mmoles of nitromethane- <i>d</i> ₃ , worked up after 5 min.	13	82	12
9.2 mmoles of nitromethane- <i>d</i> ₃ plus ^a 4.0 mmoles of <i>p</i> -toluenesulfonic acid monohydrate, worked up after 1 min.	64	36	0
B. Trityl anion			
		% (C ₆ H ₅) ₃ - CD	% (C ₆ H ₅) ₃ - CH
5.0 ml. of D ₂ O, worked up after 3 min.		49	46
9.2 mmoles of nitromethane- <i>d</i> ₃ , worked up after 2 min.		85	15
9.2 mmoles of nitromethane- <i>d</i> ₃ plus 5.8 mmoles ^a of phenol, worked up after 2 min.		55	44
9.2 mmoles of nitromethane- <i>d</i> ₃ plus 5.8 mmoles ^a of phenol, worked up after 10 min.		55	44
9.2 mmoles of nitromethane- <i>d</i> ₃ plus 4.0 mmoles ^a of <i>p</i> -toluenesulfonic acid monohydrate, worked up after 1 min.		43	57

^a The acids were mixed in a hypodermic syringe and immediately injected into the solution of the base.

obtained. Thus, the questioned^{4,5} value of the equilibrium constant for the reaction of dimethyl sulfoxide with trityl anion obtained by quenching the equilibrium mixture³ is a result of rapid deuterium exchange with solvent.

The small amount of fluorene-9,9-*d*₂ and the relatively slow changes in deuterium content with time in the experiments with fluorenyl anion and nitromethane-*d*₃ show that the proton transfer is only slowly reversible in this system. The difference in exchange rate with nitromethane and water must be due to the tremendously enhanced basicity of hydroxide¹ relative to nitromethane anion in DMSO solution. The complete absence of fluorene-9,9-*d*₂ in the reaction involving *p*-toluenesulfonic acid, and the absence of changes in deuterium content with time in the reactions of the acids with trityl anion, indicate that the proton transfers are irreversible in these systems.

In each of the experiments utilizing a mixture of acids, the product contains an amount of deuterium corresponding to equal rates of proton transfer from nitromethane, phenol, *p*-toluenesulfonic acid, and water.⁶ This is in striking contrast to the observation in aqueous solution⁷ that nitromethane reacts with hydroxide ion at a rate 10⁶ slower than does phenol.

A single simple hypothesis is capable, however, of rationalizing the present data along with a body of previously unexplained observations. If one reasonably assumes that the ionization of a carbon acid in hydroxylic solvents must involve a large amount of solvent

(4) E. C. Steiner and J. M. Gilber, *ibid.*, **85**, 3054 (1963).

(5) A. Ledwith and N. MacFarlane, *Proc. Chem. Soc.*, 108 (1964).

(6) Under the present conditions of large excess of acid, true competition should be obtained even though the reactions are probably fast in comparison to the time required for mixing.

(7) M. Eigen, *Angew. Chem. Intern. Ed. Engl.*, **3**, 1 (1964).

reorganization, and that a major part of the activation energy is connected with this solvent reorganization, whereas the ionization of an oxygen acid requires less solvent reorganization, the relative slowness of reactions of carbon acids in hydroxylic solvents is explained. On the basis of this hypothesis, we would expect that in solvents where anion solvation is unimportant solvent reorganization would not be necessary for ionization. Therefore, we should expect all proton transfers in such solvents to be diffusion controlled just as is the case with oxygen acids in aqueous solution.⁷ Previously observed large solvent isotope effects on proton transfers from carbon acids⁸ are also rationalized by this hypothesis since solvent reorganization should be easier in H₂O than in D₂O.⁹ The hypothesis, in fact, is a simple extension of Robertson's ideas on solvent reorganization accompanying solvolysis reactions.

We are currently engaged in further work to test and extend the above hypothesis.

(8) R. P. Bell, "The Proton in Chemistry," Cornell University Press, Ithaca, N. Y., 1959, p. 199.

(9) R. E. Robertson, Paper No. 20, presented at The International Symposium on Solvation Phenomena, Calgary, Alberta, Canada, Aug., 1963. Paper submitted to *Can. J. Chem.* We are grateful to Dr. Robertson for a preprint of this paper.

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Evidence for O₄. Magnetic Studies on Adsorption of Oxygen¹

Sir:

The purpose of this note is to present evidence from magnetic susceptibility data for the formation of O₄ species from O₂ at low temperatures and to elucidate the dimerization process.

Magnetic studies seeking evidence for the dimeric O₄ species in paramagnetic oxygen call for conditions of magnetic dilution. For this purpose, most workers² used mixtures of liquid oxygen and nitrogen or argon. However, this restricted the range of temperature for conducting significant magnetic studies to a few degrees below the boiling point of these mixtures (~90°K.). The studies were thus restricted mostly to the solid phase. Recently Knobler³ concluded that the "magnetic susceptibility measurements can give no unequivocal proof for the existence of a dimer." This author³ gives an excellent review of the magnetic and other physical studies in this area prior to 1961, and, as such, no extensive references to earlier work will be given in this note. Some references on spectroscopic and mass spectrometric studies on oxygen are given by Arnold, Ogryzlo, and Witzke⁴ in their most recent work on the emission bands in molecular oxygen, which seems to indicate the stabilization of O₄* and O₄ by van der Waals forces.

In our magnetic studies on oxygen, we have used a novel approach for effecting and controlling the mag-

(1) This paper was presented at the 148th National Meeting of the American Chemical Society, Chicago, Ill., Sept., 1964, and is based on work done at the Materials Research Laboratory for interdisciplinary research in chemistry, physics, planetary sciences, etc., participating in a graduate program for research in solid-state science.

(2) A. Perrier and H. K. Onnes, *Leiden Commun.*, **139d**, 48 (1914).

(3) C. M. Knobler, Doctoral Thesis, Leiden University, Leiden, 1961.

(4) S. J. Arnold, E. A. Ogryzlo, and H. Witzke, *J. Chem. Phys.*, **40**, 1769 (1964).

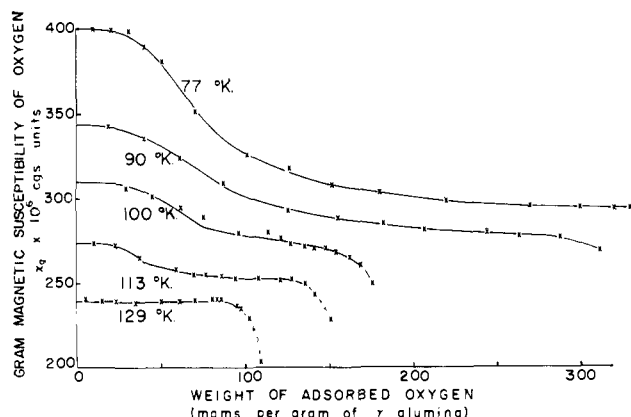


Fig. 1.—Gram magnetic susceptibility of oxygen adsorbed on γ -alumina (361 m²/g.) as a function of weight of adsorbed oxygen.

netic dilution of oxygen by adsorbing it on γ -alumina of a relatively high surface area (361 m²/g.) and thereby also extending the useful temperature range for magnetic susceptibility studies to about 40° above the boiling point of oxygen (~90°K.). This adsorption approach provided a means for studying the equilibrium 2O₂ ⇌ O₄ under conditions of a quasi-liquid phase with a greater degree of magnetic dilution than that obtained in the liquid or solid state of mixtures of oxygen and inert gas. It may be pointed out that earlier studies on adsorption of oxygen were made on supports other than alumina, and no attempts were made for a quantitative interpretation of this equilibrium.

The magnetic susceptibility of oxygen adsorbed on γ -alumina of surface area 361 m²/g. (Kaiser Aluminum and Chemical Corp., Baton Rouge, La.) was measured simultaneously with the amount adsorbed using a specially designed Faraday-type magnetic microbalance.⁵⁻⁷ The alumina was free from paramagnetic impurities and showed a constant diamagnetic susceptibility over the temperature range 77 to 373°K. Holding the temperature constant, the pressure of prepurified and dried oxygen was varied over the sample (~0.05 g.) which was outgassed under vacuum (10⁻⁷ mm.) at about 120° for several hours prior to the actual adsorption measurements. After the addition of small amounts of oxygen, measurements were made at long intervals to allow enough time to establish equilibrium between the adsorbent-adsorbate system and the surrounding gas. About 15 min. was found adequate for establishing such equilibrium. The adsorption measurements involved a direct weighing of oxygen adsorbed (accurate to within ±10 μ g.), and, as such, the difficulties of dead space and other corrections involved in volumetric methods were not encountered. The magnetic susceptibility measurements are accurate to within 1%.

A plot of magnetic susceptibility of oxygen vs. the amount of oxygen adsorbed is shown in Fig. 1 and represents the resultant of the magnetic adsorption isotherm (magnetic susceptibility vs. pressure of oxygen) and the usual adsorption isotherm (milligrams of oxygen adsorbed per gram of alumina vs. pressure). This figure shows that there is a significant decrease of about 25% in the paramagnetic susceptibility of oxygen

(5) L. N. Mulay in "Treatise on Analytical Chemistry," Vol. IV, I. M. Kolthoff and P. J. Elving, Eds., John Wiley and Sons, Inc., New York, N. Y., 1963, part I, Chapter 38.

(6) L. N. Mulay and I. L. Mulay, *Anal. Chem.*, **36**, 404R (1964).

(7) L. N. Mulay and L. K. Keys, *ibid.*, **36**, 2383 (1964).