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 acids[8] are also rationalized by this hypothesis since solvent reorganization should be easier in H_2O than in D_2O.[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.

DEPARTMENT OF CHEMISTRY　　　　　　CALVIN D. RITCHIE
STATE UNIVERSITY OF NEW YORK AT BUFFALO
BUFFALO 14, NEW YORK　　　　　　RONALD USCHOLD

Evidence for O_4.
Magnetic Studies on Adsorption of Oxygen[1]

Sir:

The purpose of this note is to present evidence from magnetic susceptibility data for the formation of O_4 species from O_2 at low temperatures and to elucidate the dimerization process.

Magnetic studies seeking evidence for the dimeric O_4 species in paramagnetic oxygen call for conditions of magnetic dilution. For this purpose, most workers[2] 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 ($\sim 90°K.$). The studies were thus restricted mostly to the solid phase. Recently Knobler[3] concluded that the "magnetic susceptibility measurements can give no unequivocal proof for the existence of a dimer." This author[3] 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 Witzke[4] in their most recent work on the emission bands in molecular oxygen, which seems to indicate the stabilization of O_4^* and O_4 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.

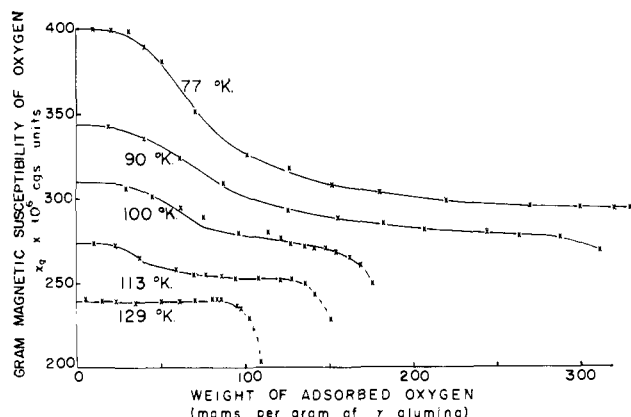(4) S. J. Arnold, E. A. Ogryzlo, and H. Witzke, *J. Chem. Phys.*, **40**, 1769 (1964).

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 m.²$/g.$) and thereby also extending the useful temperature range for magnetic susceptibility studies to about $40°$ above the boiling point of oxygen ($\sim 90°K.$). This adsorption approach provided a means for studying the equilibrium $2O_2 \rightleftharpoons O_4$ 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 m.²$/g$. (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 $\mu g.$), 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, 1. M. Kolthoff and P. J. Elving, Ed., John Wiley and Sons, Inc., New York, N. Y., 1963, part 1, Chapter 38.

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

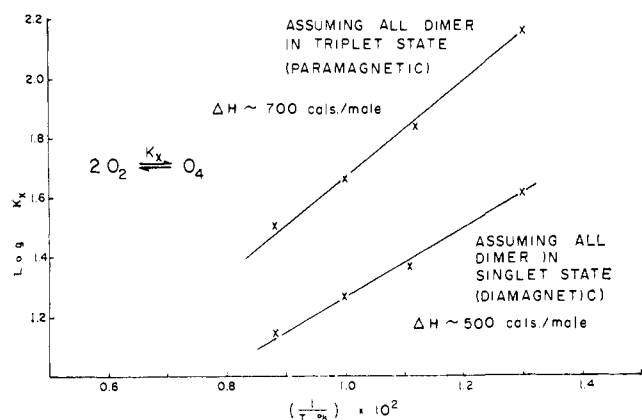(7) L. N. Mulay and L. K. Keys, *ibid.*, **36**, 2383 (1964).

Fig. 2.—Plot of log K_X (dimerization constant for $2O_2 \rightleftharpoons O_4$) as a function of reciprocal temperature assuming singlet and triplet states for the dimer.

at 77°K. over a small pressure change of 180 mm. and corresponding to an adsorption of about 340 mg. of oxygen per g. of alumina. Similar trends are observed at 90, 100, and 113°K. A simple assumption that a diamagnetic species is formed, even with very weak bonding between two oxygen molecules, helps to explain the large decrease in the paramagnetic susceptibility. Further, this appears to fit a quantitative interpretation of a dimerization equilibrium, $2O_2 \rightleftharpoons O_4$. For this system, assuming additivity of (specific) magnetic susceptibility χ, one may write

$$\chi_{obsd} = p\chi_{O_2} + (1 - p)\chi_{O_4}$$

giving

$$p = \frac{\chi_{obsd} - \chi_{O_4}}{\chi_{O_2} - \chi_{O_4}}$$

where, the subscripts obsd, O_2, and O_4 refer to the observed susceptibility and oxygen in the O_2 and O_4 form; p is the weight fraction of O_2. If O_4 is assumed to be diamagnetic, its susceptibility, of the order of 10^{-7} c.g.s. unit, may be regarded as negligible in comparison with the large paramagnetic susceptibility of oxygen ($\sim 10^{-3}$ c.g.s. unit). This gives

$$p = \chi_{obsd}/\chi_{O_2}$$

The susceptibility of O_2 corresponding to a given temperature is obtained from Van Vleck's equation.[8] Thus the weight fractions p for O_2 and $(1 - p)$ for O_4 were calculated for several points on the graph (Fig. 1), and from this the equilibrium constant K_X defined by

$$K_X = \frac{[O_4]}{[O_2]^2} = \frac{[(1 - p)/(\text{mol. wt. of } O_4)]}{[p/(\text{mol. wt. of } O_2)]^2}$$

was evaluated for each temperature.

It should be noted that the top flat region of each curve indicates existence of O_2 only and that this susceptibility agrees closely with the theoretical value. Simple calculations of surface coverage by O_2 from the known surface area of alumina and "size" of the oxygen molecule indicate a continuous formation of the dimeric species, subsequent to a certain minimum amount of adsorbed O_2 (~ 50 mg./g. of alumina). Thus the O_4 species, once formed, may be imagined

(8) J. H. Van Vleck, "Theory of Electric and Magnetic Susceptibilities," Oxford University Press, London, 1932, p. 264.

to establish an equilibrium with the O_2 molecules in all phases of adsorbed oxygen. It is evident from the curve at 129°K. that no significant dimerization can be inferred up to about 100 mg. of adsorbed oxygen. The adsorption isotherms can be interpreted in a routine manner for obtaining the heats of (physical) adsorption corresponding to the monolayer of oxygen; details of such calculations and their bearing on the heat of dimerization discussed below will be published separately, along with a quantitative explanation for the dropping-down curves (dotted lines Fig. 1) which may be attributed to intermolecular and/or intramolecular interactions in O_4.

We have evaluated the K_X values on the assumption that the adsorbed layers behave in a quasi-liquid-like manner over a certain pressure range. These values with respective standard deviations are given below. A plot of ln K_X vs. $1/T$ is shown in the lower curve in Fig. 2. The linearity of this plot is quite striking and suggests that the use of K_X in preference to some other parameter is justified in describing the quasi-liquid state of the adsorbed species: $K_X = 40.3$, $\sigma = 3.0$ (77°K., 8–50 mm.); $K_X = 22.8$, $\sigma = 1.4$ (90°K., 100–400 mm.); $K_X = 18.4$, $\sigma = 1.0$ (100°K., 250–700 mm.); $K_X = 13.9$, $\sigma = 0.60$ (113°K., 500–700 mm.)

This curve fits the well-known relation, ln $K = -\Delta H/RT +$ constant. From the slope of this curve, a ΔH of about -500 cal./mole is estimated for the heat of dimerization under the conditions of the adsorption experiments; this may not be the heat of dimerization in the purely gaseous phase or in the true liquid state, as one would like to obtain. The value obtained indeed includes some contributions from adsorption effects and also from changes in heat capacity in going from the monomer to the dimer. Refinements in the calculations of ΔH and other thermodynamic parameters are being made.

We have also interpreted the magnetic data on the assumption that the dimeric species O_4 could conceivably exist in a triplet state. For this situation the weight fraction p and the subsequent K_X values are calculated on the assumption that the specific susceptibility of O_4 (χ_{O_4}) is equal to half the specific susceptibility of O_2, since both contain two unpaired electrons per molecule. This approach gives the upper curve in Fig. 2 an estimated ΔH of about -700 cal./mole.

We propose to use our thermodynamic calculations for elucidating the respective singlet-triplet contributions to the formation of O_4. The nature of bonding in O_4 appears to involve two π-bonds of unequal energy. These aspects together with work on optical spectra and nuclear (O^{17}) and electron paramagnetic resonance spectroscopy now in progress will be published separately.[8a]

(8a) Note Added in Proof.—With reference to a report on our magnetic work which appeared in *Chem. Eng. News* [**42**, No. 36, 42 (1964)], Professor W. N. Lipscomb of Harvard University brought to our attention his recent work on γ-O_2 [*Acta Cryst.*, **17**, 777 (1964)]. In our estimate the intermolecular distances reported by him do not exclude the possibility of exchange effects sufficient to lower the paramagnetism of O_2. Further comments on the structural implications of O_4 "species" will be published separately.

[Contract AT(30-1)-2851)] for a grant which partially permitted the instrumentation described here.

MATERIALS RESEARCH LABORATORY L. N. MULAY
PENNSYLVANIA STATE UNIVERSITY L. K. KEYS
UNIVERSITY PARK, PENNSYLVANIA
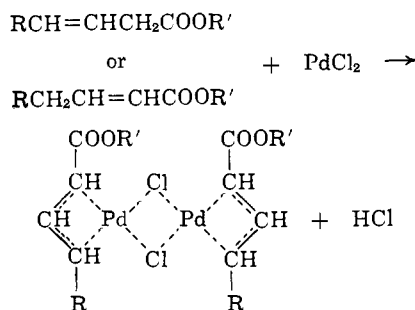RECEIVED JULY 13, 1964

Organic Syntheses by Means of Noble Metal Compounds. IX. Preparation of a New Type of π-Allylic Palladium Chloride Complex and Its Carbonylation[1]

Sir:

We have found that α,β- or β,γ-unsaturated carboxylic esters form a new type of π-allylic palladium chloride complexes as shown below. For example

$$RCH=CHCH_2COOR'$$

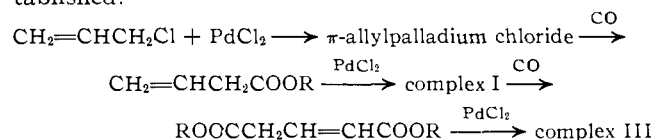$$\text{or} \qquad + \quad PdCl_2 \longrightarrow$$

$$RCH_2CH=CHCOOR'$$

1-carbethoxy-π-allylpalladium chloride (I) is formed from ethyl 2- or 3-butenoate. The complexes can be prepared either (1) by heating the esters in the presence of palladium chloride, (2) by addition of the esters into an alcoholic solution of sodium tetrachloropalladate,

are fairly consistent with the reported values of related complexes.[2]

π-Allylpalladium chloride was prepared from allyl alcohol and allyl chloride.[3] In addition, different types of compounds such as mesityl oxide[4] and 2-methyl-1-pentene[5] were found to form π-allylic complexes of palladium chloride, and, in these cases, the absence of a hydrogen at a central carbon atom of the complexes was regarded as essential. Now, it has been established by the present studies that a compound having an allylic hydrogen activated by a carbonyl group can form the 1-carboxy-π-allylic complex with evolution of hydrogen chloride.

Carbonylation of π-allylpalladium chloride in ethanol to form ethyl 3-butenoate is known,[1,6,7] and it is reasonable to expect that any π-allylic complexes of palladium chloride can be carbonylated under similar conditions. Actually the complexes obtained here were found to be carbonylated to give unsaturated esters. Thus the complex I afforded ethyl glutaconate as a main product. Furthermore, having allylic hydrogens activated by the carbethoxy group, ethyl glutaconate can form the complex III. Thus, the following sequence of complex formation and carbonylation reactions has been established.

$$CH_2=CHCH_2Cl + PdCl_2 \longrightarrow \text{π-allylpalladium chloride} \xrightarrow{CO}$$

$$CH_2=CHCH_2COOR \xrightarrow{PdCl_2} \text{complex I} \xrightarrow{CO}$$

$$ROOCCH_2CH=CHCOOR \xrightarrow{PdCl_2} \text{complex III}$$

Further work is in progress on the extension of the above sequence of the reactions by carbonylating the complex III, followed by complex formation.

TABLE I

PHYSICAL PROPERTIES OF THE COMPLEXES

Starting material	R₂	Complex R₃ R₄ R₅			M.p., °C.	Mol. wt., found (calcd.)	Analysis, %, found (calcd.) C	H	Cl	Chemical shift τ₁ τ₂ τ₃ τ₄				Coupling, c.p.s. J₁₂ J₁₃ J₁₄		
Ethyl 2- and 3-butenoate	I H	H	H	CO₂Et	141–143	497.6 (509.9)	28.44 (28.26)	3.60 (3.56)	14.08 (13.90)	3.90 5.80 6.71 6.36				7.2 12.5 11.3		
Ethyl 3-pentenoate	II H	CH₃	H	CO₂Et	140–150 dec.	527.4 (537.8)	31.35 (31.25)	4.11 (4.12)	13.21 (13.19)	4.10 5.78 ... 6.56				6.9 ... 10.5		
Diethyl glutaconate	III CO₂Et	H	H	CO₂Et	175–176	658.8 (654.1)	33.29 (33.05)	4.01 (4.09)	10.84 (10.89)	3.25 ... ... 6.10				11.5		
CH₂=CHCH₂Cl[2]	H	H	H	H						4.55 5.98 7.05 ...				7.1 12.1 ...		

or (3) by addition of the esters into a benzene solution of bisbenzonitriledichloropalladium. The complexes are yellow crystalline substances and most of them are moderately soluble in ordinary organic solvents. The π-allylic structure was assigned to the complexes on the basis of molecular weights, elemental analyses, and n.m.r. spectra shown in Table I. The most convincing evidence was obtained from the n.m.r. spectra (in CDCl₃). Their τ-values and coupling constants (J)

(1) Part VIII: J. Tsuji, J. Kiji, S. Imamura, and M. Morikawa, *J. Am. Chem. Soc.*, **86**, 4350 (1964).

(2) S. D. Robinson and B. L. Shaw, *J. Chem. Soc.*, 4806 (1964); B. L. Shaw, *Chem. Ind.* (London), 1190 (1962).

(3) J. Smidt and W. Hafner, *Angew. Chem.*, **71**, 284 (1959).

(4) G. W. Parshall and G. Wilkinson, *Chem. Ind.* (London), 261 (1962).

(5) R. Hüttel and H. Christ, *Chem. Ber.*, **96**, 3101 (1963).

(6) J. Tsuji, J. Kiji, and M. Morikawa, *Tetrahedron Letters*, **No. 26**, 1811 (1963).

(7) W. T. Dent, R. Long, and G. H. Whitfield, *J. Chem. Soc.*, 1588, 1852 (1964).

BASIC RESEARCH LABORATORIES JIRO TSUJI
TOYO RAYON CO. SHINZO IMAMURA
KAMAKURA, JAPAN JITSUO KIJI
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