$[Co(en)_3]^{3+}$ with OH^-, Cl^-, and SO_4^{2-} by an independent method.[7] However, it should be noted that spectrochemical effects need not necessarily be in the same order as thermodynamic association constants, and, of course, the effects of the different electrolytes are not the same for the two CD bands.

(7) D. R. Stranks, "Advances in the Chemistry of the Coordination Compounds," S. Kirschner, Ed., Macmillan Co., New York, N.Y., 1961, p 574.

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Radiolysis in the Adsorbed State[1]

Sir:

Studies of the decomposition by γ-rays of molecules adsorbed on chemically inert mineral supports[2-6] have shown that excitation energy delivered to the solid from the radiation can migrate to the surface and become available for decomposition of the adsorbate. For a further study of this process, we have selected azoethane, $(C_2H_5)_2N_2$, as adsorbate, since the chief decomposition product, nitrogen, is readily separated and measured. Minor gaseous products, hydrogen and methane, which separate with the nitrogen and are measured simultaneously, serve as indicators of the occurrence of other modes of decomposition which presumably require more energy than needed for the production of nitrogen. Radiolysis of pure liquid azoethane gave $G(N_2) = 3.69$, $G(H_2) = 0.46$, and $G(CH_4) = 0.076$.
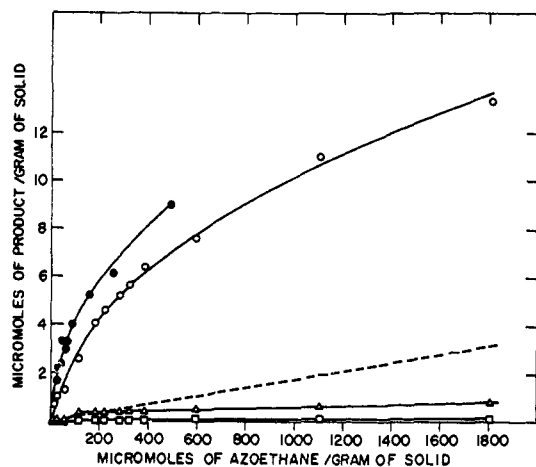

Fig. 1.—Radiolysis products of azoethane adsorbed on silica gel, Co^{60} γ-rays, dose 5.9 Mrads: open symbols, Fisher Scientific Co. gel, surface 775 m.^{2}/g. determined by the B.E.T. method using N_2; solid symbols, gel heated to 800° in air for 16 hr., surface 500 m.^{2}/g.; circles, N_2; triangles, H_2; squares, CH_4; dotted line is "expected" nitrogen yield (see text).

When adsorbed on silica gel and radiolyzed (Fig. 1), azoethane behaved much like pentane.[2,3] As the amount of azoethane on the gel was increased, the amount of product formed increased, very rapidly at first, more slowly at higher coverages. The dotted

(1) Research performed under the auspices of the U. S. Atomic Energy Commission.
(2) J. M. Caffrey, Jr., and A. O. Allen, *J. Phys. Chem.*, **62**, 33 (1958).
(3) J. W. Sutherland and A. O. Allen, *ibid.*, **64**, 1040 (1960).
(4) R. Coekelbergs, A. Crucq, A. Frennet, J. Decot, and L. Timmerman, *J. chim. phys.*, **60**, 51 (1963).
(5) R. R. Hentz, *J. Phys. Chem.*, **66**, 1625 (1962).
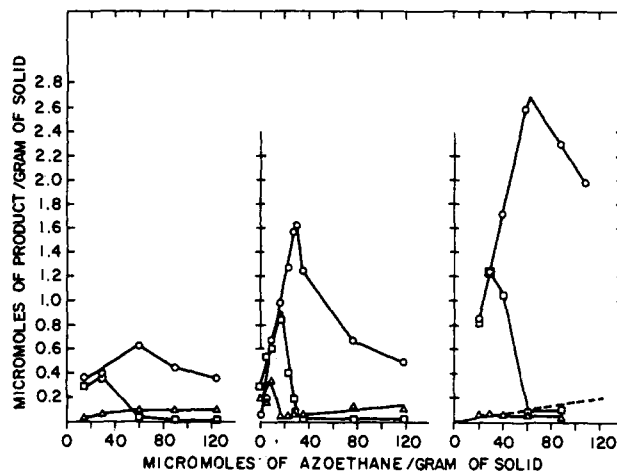(6) W. H. Clingman, Jr., *Ind. Eng. Chem.*, **52**, 72 (1960).

Fig. 2.—Radiolysis products of azoethane adsorbed on magnesium oxide, Co^{60} γ-rays, dose 5.9 Mrads: left, oxide prepared by heating basic carbonate in air for 16 hr. to 600°; center, to 800°; right, to 1140° (meaning of symbols as in Fig. 1).

"liquid line" shown in the figures represents the amount of nitrogen that would be formed if only the energy absorbed by the azoethane were effective in decomposing it and the yield of nitrogen were the same as for the liquid. That the actual yield of nitrogen is many times greater than that shown by the liquid line indicates transfer of energy from the solid. An interesting observation was made during the blank runs. Silica gel irradiated to 6 Mrads under vacuum turns blue. Simply on exposure to azoethane vapor, the blue color immediately disappeared, while nitrogen was evolved to the extent of about 10% of what would have formed if the azoethane had been present during the irradiation. Similar observations are reported by Kohn and by Hentz.[7] That practically all the color centers interact with the added material seems less surprising if we remember that, in silica gel, practically all the solid lies within two atomic diameters of the surface.

With magnesium oxide the results were more unexpected (Fig. 2). Three preparations were heated to different temperatures. Surface determination of the two higher temperature preparations, by the B.E.T. method using nitrogen, gave 29 m.^{2}/g. for both. It is known, however,[8] that the higher calcination temperature yields an oxide of less imperfect crystalline structure and lower energy. Figure 2 shows that, at low coverages, extensive energy transfer to azoethane occurs, the efficiency being greater the more perfect the crystal lattice. Most striking, however, is the decline at higher coverages of the total amount of decomposition. Thus additional azoethane not only fails to decompose but protects the first molecules adsorbed against decomposition. The amount of azoethane required for maximum yield is quite different for the different gaseous products, being higher for nitrogen than for methane. Hydrogen exhibited a maximum at a still lower amount of azoethane for the sample of magnesium oxide prepared at 800°. The decline sets in well below complete monolayer coverage, which should occur at around 120 μmoles/g. if the area per adsorbed azoethane molecule is assumed

(7) (a) H. W. Kohn, *Nature*, **184**, 630 (1959); (b) R. R. Hentz, *J. Phys. Chem.*, **66**, 2714 (1962).
(8) R. Fricke and J. Lueke, *Z. Elektrochem.*, **41**, 174 (1935); R. M. Dell and S. W. Weller, *Trans. Faraday Soc.*, **55**, 2203 (1959).

to be about 40 Å.[2]. Limited data obtained at different total doses show that for constant coverage the G values decrease somewhat with increasing dose, but the nature of the curves of yield vs. coverage at constant dose does not seem to be greatly affected.

We believe the adsorbate molecules interact with a surface state which can draw excitation energy from a considerable volume of the solid. On magnesia, the data appear to suggest that the available energy is divided among the molecules present, so that at low coverages some molecules are raised to high states of excitation, while at higher coverages only states of lower energy are formed. Thus with increasing coverage, hydrogen, which requires most energy for its formation, decreases first, then methane, and finally nitrogen, when the average excitation energy available per molecule becomes too small to produce decomposition. The energy available to the surface increases with decreasing lattice imperfections, because fewer traps are then present to compete with the surface states for the energy of the electrons in the conduction band. Decrease in the yield with increasing dose may be due to production of disorder in the crystal by the radiation.[9]

We have also studied azoethane radiolysis on graphite, and on the semiconductors zinc oxide and nickel oxide. The results differ in detail, but in all cases the apparent amount of energy transfer is much less than with the insulators, silica and magnesia. This is as expected, since the quantum of excitation energy transferred to an adsorbate molecule from the solid cannot be much larger than the band gap in the solid.

(9) R. Smoluchowski and D. A. Wiegand, Discussions Faraday Soc., 31, 151 (1961).

(10) NATO Research Fellow, 1963–1964.

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Spin–Spin Coupling in Binuclear Complexes

Sir:

The mechanism of spin–spin coupling of the unpaired electrons on adjacent metal ions in binuclear complexes is a currently debated topic. Recently, Forster and Ballhausen[1] have calculated the overlap integrals for the σ- and δ-orbitals of the copper ions in dimeric copper acetate monohydrate using a molecular orbital scheme and have concluded that the Cu–Cu interaction results from the formation of a σ-bond. Figgis and Martin[2] and Ross[3] had previously attributed the antiferromagnetism in this compound to the formation of a δ-bond. Boudreaux[4] has re-examined the problem from a molecular orbital viewpoint and notes that a more sophisticated treatment tends to favor the δ-bond model. An alternate explanation for the phenomenon would invoke a super-exchange mechanism operating through the bridging groups. This latter mechanism has been suggested, for example, for a binuclear Schiff base complex of copper(II).[5] We now wish to report

(1) L. S. Forster and C. J. Ballhausen, Acta Chem. Scand., 16, 1385 (1962).

(2) B. N. Figgis and R. L. Martin, J. Chem. Soc., 3837 (1956).

(3) I. G. Ross, Trans. Faraday Soc., 55, 1057 (1959).

(4) E. A. Boudreaux, Inorg. Chem., 3, 506 (1964).

(5) G. A. Barclay, C. M. Harris, B. F. Hoskins, and K. Kokot, Proc. Chem. Soc., 264 (1961).

magnetic data for a series of 4-substituted pyridine N-oxide complexes of copper(II) halides which can best be interpreted in terms of the super-exchange model. This is the first demonstration of a spin–spin coupling mechanism for a situation for which either model might have been applicable.

The temperature dependence of the magnetic susceptibility of the 1:1 complex of pyridine N-oxide with copper chloride has been reported by Harris and co-workers,[6] and the suggested binuclear structure with oxygen bridges has recently been confirmed.[7] We have prepared a series of complexes of pyridine N-oxide with substituents of $-NO_2$, $-H$, $-CH_3$, $-Cl$, and $-OH$ in the 4-position of the pyridine ring with either copper chloride or copper bromide[8] and have determined the temperature dependence of the magnetic susceptibilities in the temperature range 195–$350°K$. Below $195°$, the triplet state was in most cases not appreciably populated, and above $350°$ the compounds usually decomposed. The energy separation between the ground state singlet and excited state triplet was evaluated by the method that has been used previously,[9,10] and the data are presented in Table I. As is shown in Table I the exchange energy is markedly

TABLE I

Magnetic Properties of $R-\!\!\langle\bigcirc\rangle\!\!-N\!-\!O{\cdot}CuX_2$

R	X	ΔH, cm.$^{-1}$	σ_R	σ^a
NO_2	Br	143	+0.65	+0.778
H	Cl	616	0.0	0
CH_3	Cl	986	−0.11	−0.17
Cl	Cl	1090	−0.24	+0.227
OH	Cl	2150	−0.60	−0.37

^{a} J. Hine, "Physical Organic Chemistry," 2nd Ed., McGraw-Hill Book Co., New York, N. Y., 1962.

dependent upon the substituent on the pyridine ring and correlates well with the substituent constant σ_R.[11] As the σ_R-value of the substituent decreases, the electron density in the π-orbitals of the bridging oxygen atoms increases. This permits an increased interaction between the unpaired electrons in the π-orbitals of the copper ions and the oxygen π-electrons. The enhancement of the exchange interaction by the greater electron density in these oxygen π-orbitals is reflected by the ΔH values. If spin–spin coupling occurred by the metal–metal bond mechanism, the substituent would not have such a pronounced effect on the exchange energy, and the substituent effect would correlate with the Hammett σ-value. This effect will be treated in a forthcoming publication.

(6) C. M. Harris, K. Kokot, S. L. Lenzer, and T. N. Lockyer, Chem. Ind. (London), 651 (1962).

(7) J. C. Morrow and H. L. Schäfer, private communication.

(8) The preparation and characterization of these and other similar compounds will be reported elsewhere with Prof. H. B. Jonassen and Dr. Y. Muto.

(9) R. C. Stouffer, D. H. Busch, and W. B. Hadley, J. Am. Chem. Soc., 83, 3732 (1961).

(10) W. E. Hatfield, T. S. Piper, and U. Klabunde, Inorg. Chem., 2, 629 (1963).

(11) $\sigma_R = \sigma - \sigma_I$