

to be about 40 \AA^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.

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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 Ballhausen¹ 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 Martin² and Ross³ had previously attributed the anti-ferromagnetism in this compound to the formation of a δ -bond. Boudreaux⁴ 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

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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 $-\text{NO}_2$, $-\text{H}$, $-\text{CH}_3$, $-\text{Cl}$, and $-\text{OH}$ in the 4-position of the pyridine ring with either copper chloride or copper bromide⁸ 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 $\text{R}-\text{C}_5\text{H}_4\text{N}-\text{O}-\text{CuX}_2$

R	X	$\Delta H, \text{cm.}^{-1}$	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.

Acknowledgments.—The authors wish to acknowledge support of this research by the donors of the Petroleum Research Fund which is administered by the American Chemical Society, by the University Research

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

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Activation Energy of Deuterium-Hydrogen Exchange in Amides

Sir:

When it was found that deuterium exchange rates with protein N-H groups fall roughly into two classes, rapid and slow,^{1,2} it seemed reasonable to assign the fast group to unfolded portions of the polypeptide chain and the slow group to helical sections.³ On this basis one could ascribe the measured heat of activation of 20 kcal./mole for the slow exchange to the need to open three adjacent hydrogen bonds in order to unfold a helical segment,³ each hydrogen bond presumably requiring 6-8 kcal. It was assumed in this connection that unfolded sections of the polypeptide chain exchanged hydrogens with a greatly reduced heat of activation.

As far as we can find no actual measurements have been made of the activation energy for deuterium-hydrogen exchange in a simple, solvated N-H group. In the course of studies of catalytic effects on such exchanges,⁴ we have examined, therefore, the effect of temperature on the kinetics of deuterium exchange in a model amide, N-methylacetamide, $\text{CH}_3\text{CONHCH}_3$, when it is entirely in the monomeric state.

Exchange rates were followed for solutions of 1 M N-methylacetamide in D_2O by observation of changes in absorbance at 1.43μ in the near-infrared region of the spectrum. It was found immediately at room temperature that the rate of exchange was acid- and base-catalyzed, in agreement with the report of Nielsen.⁵ Experiments were then extended to lower and higher temperatures, over the pD range 4.5-6.5.

In the range pD 4.5-5.5, the exchange was acid-catalyzed at each of three temperatures, 12, 24, and 32° . The activation energy (Fig. 1), calculated from the temperature coefficient of the rate constant at pD 5.0, is 17 kcal./mole. The rate reaches a minimum at approximately pD 5.5. Above pD 5.5 it is base-catalyzed, and rate constants were measured over the range pD 5.5-6.5. Data at pD 6.3 (Fig. 1) were used to calculate the activation energy, and a value of 23 kcal./mole was obtained. Essentially the same energies would be obtained for other pD's in the acid or basic range, respectively. The observed rates at pD values more than 0.5 unit below or above the pD of the minimum rate were greater than 90% acid- or base-catalyzed, respectively.

It seems clear, therefore, that at least in this model of a peptide group, $\text{CH}_3\text{CONHCH}_3$, a substantial activation energy (near 20 kcal./mole) is essential for exchange with deuterium even when the N-H is not hydrogen bonded to a C=O. If additional energy

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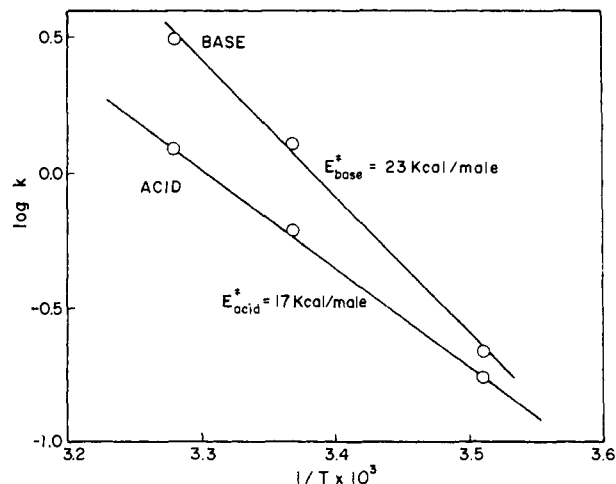


Fig. 1.—Logarithm of the observed rate constant (in min.^{-1}) for the deuterium exchange of D_2O with the N-H hydrogen of $\text{CH}_3\text{CONHCH}_3$, as a function of temperature. Acid constants at pH 5.0; base constants at pH 6.3.

is needed to break hydrogen bonds in a helix before exchange occurs, then the observed activation energy for the over-all exchange process ought to be substantially greater than 20 kcal./mole.

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X-Ray Structure Determination of Cubane¹

Sir:

We wish to present the results of a high-precision X-ray analysis as absolute confirmation of the structural assignment of the recently synthesized hydrocarbon cubane.²

The space group of cubane³ is $R\bar{3}$ with the cell constants $a = 5.340 \pm 0.002 \text{ \AA}$. and $\alpha = 72.26 \pm 0.05^\circ$. There is one molecule per unit cell.

Three-dimensional X-ray data were collected with Cu $K\alpha$ radiation on a GE XRD-5 instrument with a scintillation counter employed as a detector. The intensities were collected using the moving counter-moving crystal technique. The 97 independent structure amplitudes were obtained by averaging the three reflections related by the crystal's threefold axis.

A body diagonal carbon and the atom related to it by the center of symmetry are at special positions on a threefold axis at x, x, x and $\bar{x}, \bar{x}, \bar{x}$. The hydrogens attached to these carbons also lie on this special position. The other carbons and hydrogens, six of each, occupy the general positions of the space group. The coordinates of the independent atoms and the temperature factors for the atoms are given in Tables I and II.

(1) This research was supported by a Public Health Service Grant.

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(3) (a) The crystals were grown by sublimation with material supplied by P. Eaton; (b) No. 148, International Tables for X-ray Crystallography.