

dithiacyclopentyl case and little participation in the methylmercapto case, seems quite interesting. Probably, five-membered ring structures at transition states such as VII, VIII, and IX are suited for efficient participation, while four-membered ones, like X, are not.

Acetolysis of the corresponding tosylates gave similar results. The only exception is in the case of *o*-dithiacyclopentyl tosylate<sup>5</sup> which gave no acetate but produced very stable salts<sup>6</sup> on adding potassium iodide or lithium perchlorate to the reaction mixture. Structural determination of this salt is now in progress.

(5) The proton nmr spectrum of this compound exhibits signals at  $\tau$  2.46 (m, 4 H, aromatic), 2.75 (m, 4 H, aromatic), 4.33 (s, 1 H, CH), 4.79 (s, 2 H, CH<sub>2</sub>), 6.64 (m, 4 H, CH<sub>2</sub>CH<sub>2</sub>), and 7.58 (s, 3 H, CH<sub>3</sub>).

(6) Iodide decomposed at 138°. *Anal.* Calcd for C<sub>10</sub>H<sub>11</sub>SiI: C, 37.27; H, 3.45. Found: C, 36.92; H, 3.58. Perchlorate decomposes at 157°. Both salts showed identical proton nmr spectrum.

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### Evidence for Hydroxyl-Group Abstraction by Hydrogen Atoms

Sir:

It has been shown<sup>1</sup> that hydrogen atoms of thermal energies are capable of abstracting hydrogen atoms from hydrocarbons in the solid state. Abstraction and replacement of halogen atoms has also been demonstrated.<sup>2</sup> Herak and Gordy<sup>3</sup> showed that various groups, too, can be replaced by thermal hydrogen atoms. However, abstraction of groups has not been observed, except for the amino group in alanine.<sup>4</sup> In this study we present the evidence that hydroxyl groups can also be abstracted by hydrogen atoms. Powdered alloxan, which is known to be in the dihydroxy form,<sup>5</sup> was exposed to the beam of thermal hydrogen atoms at room temperature in a chamber described elsewhere.<sup>6</sup> The produced radicals were studied with electron spin resonance. Figure 1 shows the spectrum of alloxan previously exposed to H atoms (upper curve) in comparison to the resonance of the  $\gamma$ -irradiated specimen (middle line). It is obvious that the same radicals are present in both samples. They have been identified as the  $>\dot{C}-OH$  radicals.<sup>7</sup> The asymmetry of the resonance line is due to the large anisotropy of the hydroxyl-proton hyperfine splitting. The spectrum of the irradiated single crystal of alloxan (lower curve) clearly demonstrates the presence of the hydroxyl-proton coupling.

No essential difference in the resonance pattern was observed if deuterium atoms instead of hydrogen were used. This fact demonstrates that addition of hydrogen atoms does not take place. Thus, the observed radicals

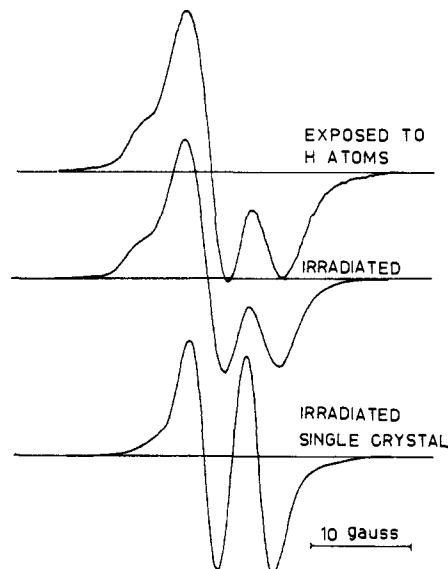
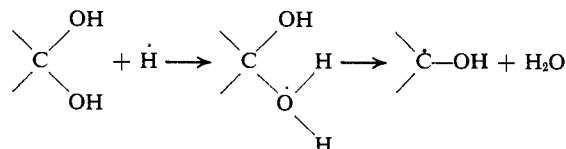


Figure 1. Electron spin resonance spectra (first-derivative curves) of alloxan, exposed to hydrogen atoms (upper curve), irradiated (middle curve), and  $\alpha$ -irradiated single crystal (lower curve).

are formed by abstraction of one of the hydroxyl groups. The reaction with hydrogen atoms probably goes as follows.



First, the unstable complex is formed which then transforms into the radical and a water molecule. The detailed mechanism, however, is not completely understood. It is not known whether  $n$  or  $\pi$  electrons of the hydroxyl group participate in the complex formation. In any case, the hydroxyl group must be in the excited state to react with an H atom. Since the first excited state of  $n$  electrons is lower than that of  $\pi$  electrons, it is believed that  $n$  electrons take part in the complex formation.

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### The Alkaline Hydrolysis of 5-Nitrocoumaranone. A Method for Determining the Intermediacy of Carbanions in the Hydrolysis of Esters with Labile $\alpha$ Protons

Sir:

There has recently been a suggestion that certain esters possessing readily ionizable protons adjacent to the carbonyl function might hydrolyze in alkaline solution *via* a pathway with either an isocyanate<sup>1</sup> or a ketene<sup>2</sup> intermediate (eq 1) rather than the well-known tetrahedral intermediate. In these investigations, however, no direct method was proposed to distinguish eq 1

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- (2) T. C. Bruce and B. Holmquist, *J. Amer. Chem. Soc.*, **90**, 7136 (1968).

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- (2) J. N. Herak and W. Gordy, *Proc. Natl. Acad. Sci., U. S.*, **55**, 1354 (1966).
- (3) J. N. Herak and W. Gordy, *J. Am. Chem. Soc.*, **89**, 3818 (1967).
- (4) W. Snipes and J. Schmidt, *Radiation Res.*, **29**, 194 (1966).
- (5) J. F. Thorpe and M. A. Whiteley, "Thorpe's Dictionary of Applied Chemistry," Vol. 1, 4th ed, Longmans Green and Co., London, 1947, p 243.
- (6) J. N. Herak, *Rev. Sci. Instr.*, **38**, 1669 (1967).
- (7) M. Kashiwagi, *J. Mol. Spectry.*, **20**, 190 (1966).

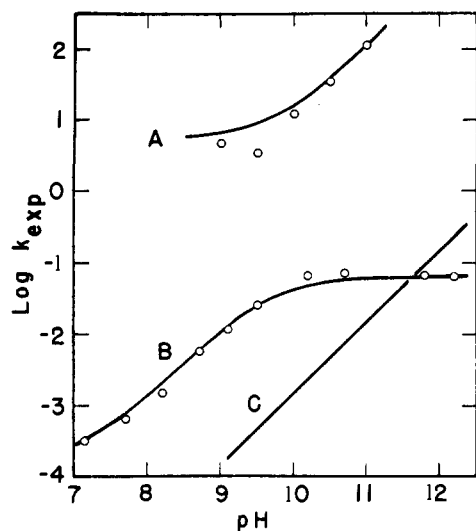
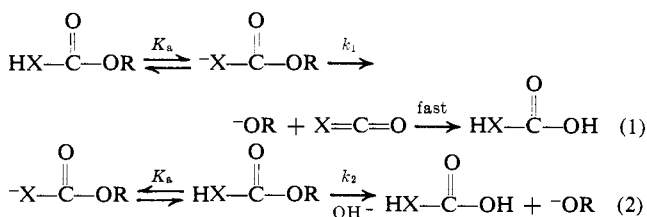


Figure 1. Observed rate constants in the hydrolysis and ionization of 5-nitrocoumaranone (L). Open circles are experimental points obtained from extrapolation to zero buffer concentration and 0.2 *M* ionic strength. (A) Rates of ionization of L; line based on  $k_{\text{obsd}} = [1 + (1.89 \times 10^{-10} M)/(H)]/0.18 \text{ sec}$ . Errors in the experimental points are estimated to be  $\pm 30\%$ . (B) Rates of appearance of product A; line based on  $k_{\text{obsd}} = 1.57 \times 10^{-1} + (6.5 \times 10^{-2} \text{ sec}^{-1})/[1 + (H)/1.98 \times 10^{-10} M]$ . (C) Rate of hydrolysis of *p*-nitrophenylacetate for comparison;  $k_{\text{OH}} = 14 M^{-1} \text{ sec}^{-1}$ .

from eq 2, the latter pathway going through a tetra-



hedral intermediate but complicated by the formation of nonproductive ionized reactant.

These two schemes predict a sigmoid dependence of  $k_{\text{exptl}}$  (the observed first-order rate constant for production of alcohol or alcoholate product) with pH (see eq 3 and 4), and thus observation of this dependency is no indication of pathway. To date the best indirect evidence for eq 1 has been the comparison of the hydrolytic rate constants of chemically very similar esters differing only in their possession or lack of readily ionizable protons  $\alpha$  to the carbonyl function.<sup>1,2</sup>

We have found that, if the ester is completely ionized, then on the basis of solvent isotope effects one may distinguish experimentally between eq 1 and 2.<sup>3</sup> From these schemes, if the carbanion is in rapid equilibrium with the ester at all pH values (the condition for observing first-order kinetics at all pH values), one may derive eq 3 and 4, respectively, for  $k_{\text{exptl}}$ . Equation 3 states

$$k_{\text{exptl}} = \frac{k_1}{1 + \frac{(H)}{K_a}} \quad (3)$$

$$k_{\text{exptl}} = \frac{k_2 K_w}{K_a \left[ 1 + \frac{(H)}{K_a} \right]} \quad (4)$$

(3) For incompletely ionized esters, the comparison of the rates of hydrolysis with the rates of deuteration can distinguish between the two schemes: P. Mueller, D. F. Mayers, O. R. Zaborsky, and E. T. Kaiser, to be published.

that in strongly alkaline solution ( $\text{pH} \gg \text{p}K_a$ )  $k_{\text{exptl}}$  will be equal to  $k_1$ . Since the elimination step of eq 1 does not involve a proton transfer,  $k^{\text{D}_2\text{O}}_{\text{exptl}}/k^{\text{H}_2\text{O}}_{\text{exptl}} = 1$ . In the same conditions, eq 4 and 2 yield  $k^{\text{D}_2\text{O}}_{\text{exptl}}/k^{\text{H}_2\text{O}}_{\text{exptl}} = [k_2^{\text{D}_2\text{O}}/k_2^{\text{H}_2\text{O}}][K_w^{\text{D}_2\text{O}}/K_w^{\text{H}_2\text{O}}][K_a^{\text{H}_2\text{O}}/K_a^{\text{D}_2\text{O}}]$ . Using values of  $k^{\text{D}_2\text{O}}/k^{\text{H}_2\text{O}} = 1.22$ ,<sup>4</sup>  $K_w^{\text{D}_2\text{O}}/K_w^{\text{H}_2\text{O}} = 0.15$ , and  $K_a^{\text{H}_2\text{O}}/K_a^{\text{D}_2\text{O}} = 3.5$ ,<sup>5</sup> we estimate that  $k^{\text{D}_2\text{O}}_{\text{exptl}}/k^{\text{H}_2\text{O}}_{\text{exptl}}$  should be approximately 0.65. Thus eq 1 and 2 should be clearly distinguishable experimentally. Similar calculations show that if  $\text{pH} \leq \text{p}K_a$  both pathways predict approximately equal kinetic solvent isotope effects.

As a first application of this method, we have investigated the hydrolysis of 5-nitrocoumaranone (L).<sup>6</sup> This lactone is ideally suited to this purpose because of its ease of hydrolysis, the strong absorption at 400  $m\mu$  of its hydrolysis product, and its expected ionizability.<sup>7</sup>

In alkaline solution the hydrolysis of L is clearly a biphasic reaction: at 400  $m\mu$  a rapid first-order burst of absorbance is followed by a much slower first-order appearance of the product acid A. At 500  $m\mu$ , where A and L do not absorb appreciably, a rapid first-order increase followed by a slower first-order decrease in optical density is observed. At 400  $m\mu$  and at 500  $m\mu$  the two fast reactions had identical rate constants, as did the two slower reactions. At whatever pH the reaction was observed the initial burst at 400  $m\mu$  was never greater than 10% of the final absorbance. First-order rate constants as a function of pH for both the fast and slow reactions are given in Figure 1, curves A and B, respectively. The pH dependency of the slow reaction, curve B, can be interpreted as being formally dependent on a base of  $\text{p}K_a = 9.7$ . Curve C of Figure 1 is, for comparison, the rate of hydrolysis of *p*-nitrophenylacetate as a function of pH. These facts establish that only one intermediate is kinetically significant in the hydrolysis of L to A, that the transient intermediate I is always formed much faster than the product A, and that I is in a pH-dependent equilibrium with L.

The  $\text{p}K_a$  of I was also determined by extrapolating the decay of absorbance at 500  $m\mu$  back to zero time at various pH values. These measurements gave a sigmoid dependence of absorbance with pH, interpreted to give  $\text{p}K_a = 9.8$ ,  $\epsilon_{\text{lim}} = 700$ , indistinguishable from the  $\text{p}K_a$  determined kinetically (for comparison, the  $\text{p}K_a$  of 5-nitro-2-indanone was measured to be 8.94 in water and 9.48 in deuterium oxide). Finally, the similarity of the rate constant for ionization of L with that for acetylacetone<sup>8</sup> and the fact that L hydrolyzed to A in  $\text{D}_2\text{O}$  gave no methylene signal in an nmr instrument establish the structure of I as the carbanion formed from L by loss of an  $\alpha$  proton.

With this information in hand either eq 1 or eq 2 adequately describe the observed hydrolysis. Measurement of the kinetic solvent isotope effect at 0.01 *M* lyate ion, 0.2 *M* KCl, in  $\text{D}_2\text{O}$  and  $\text{H}_2\text{O}$  yields  $k^{\text{D}_2\text{O}}_{\text{exptl}}/k^{\text{H}_2\text{O}}_{\text{exptl}} = 0.58$ , consistent with the prediction made

(4) Determined by measuring the rate of hydrolysis of *p*-nitrophenylacetate in  $\text{H}_2\text{O}$  and  $\text{D}_2\text{O}$  at identical lyate concentration.

(5) R. P. Bell, "The Proton in Chemistry," Cornell University Press, Ithaca, N. Y., 1959, p 188.

(6) Prepared by the method of P. Tobias, J. H. Heidema, K. W. Lo, E. T. Kaiser, and F. J. Kézdy, *J. Amer. Chem. Soc.*, **91**, 202 (1969).

(7) The close analog 5-nitro-2-indanone is known to readily give a carbanion in aqueous solution with a characteristic red color (F. Heusler and H. Schieffer, *Ber. Deut. Chem. Ges.*, **32**, 28 (1899)).

(8) M. Eigen and G. G. Hammes, *Advan. Enzymol.*, **25**, 1 (1963).

from eq 4 but not from eq 3. Thus application of the method described above for discriminating between pathways 1 and 2 clearly shows that the latter is the route for the hydrolysis of 5-nitrocoumaranone.

The generality of eq 2 as the pathway for the hydrolysis of readily ionizable esters such as 5-nitrocoumaranone is difficult to assess. Since aryl *N*-monoalkylcarbamate esters hydrolyze  $10^6$  times faster than aryl *N,N*-dialkylcarbamate esters<sup>9</sup> eq 1 is the most likely pathway for the hydrolysis of the former compounds. Consideration of the resonance involved in the carbanion described here, carbamate esters, and the structures of isocyanates and ketenes leads to the conclusion that there are enough structural differences between aryl *N*-monoalkylcarbamate esters and readily ionizable lactones so that they could easily hydrolyze *via* different pathways.

The excellent agreement of the predicted and observed kinetic solvent isotope effects makes this method very attractive for the investigation of carbanion-catalyzed hydrolyses.

**Acknowledgment.** This investigation was supported by Public Health Service Research Grant No. GM-13885 from the National Institutes of Health.

(9) L. W. Dittert, Ph.D. Dissertation, University of Wisconsin, 1961; *Dissertation Abstr.*, **22**, 1837 (1961).

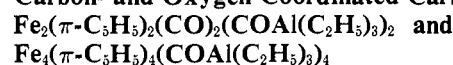
(10) Public Health Service Predoctoral Trainee.

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### Carbon- and Oxygen-Coordinated Carbon Monoxide.



Sir:

While many compounds are known in which cyanide is coordinated through carbon and nitrogen,<sup>1</sup> the iso-electronic CO ligand has been known to bond only through carbon. We report here the first examples of carbon monoxide coordinated through both carbon and oxygen.

Addition of a slight excess of  $\text{Al}_2(\text{C}_2\text{H}_5)_6$  to a benzene solution of  $\text{Fe}_2(\pi\text{-C}_5\text{H}_5)_2(\text{CO})_4$ <sup>2</sup> produces immediate lightening of the red solution. Bright red crystals of  $\text{Fe}_2(\pi\text{-C}_5\text{H}_5)_2(\text{CO})_4 \cdot 2\text{Al}(\text{C}_2\text{H}_5)_3$  are obtained by addition of heptane followed by partial removal of solvent.<sup>3</sup> *Anal.* Calcd for  $\text{C}_{26}\text{H}_{40}\text{Al}_2\text{Fe}_2\text{O}_4$ : C<sub>2</sub>H<sub>5</sub>, 28.22; Fe, 19.2. Found: C<sub>2</sub>H<sub>5</sub> (by hydrolysis), 28.64; Fe, 20.5. The parent compound,  $\text{Fe}_2(\pi\text{-C}_5\text{H}_5)_2(\text{CO})_4$ , is nearly quantitatively regenerated upon hydrolysis or reaction with trimethylamine. Experiments conducted on the vacuum line demonstrate that no gases, such as CO, are evolved upon reaction of aluminum trialkyl with the iron dimer. Nmr chemical shifts are  $\tau$  5.62 (singlet), 8.43 (triplet), and 9.51 (quartet) with relative intensities 9.6:18:13.1. The expected ratios are 10:18:12 for C<sub>5</sub>H<sub>5</sub>, CH<sub>3</sub>, and CH<sub>2</sub>, respectively.

(1) D. F. Shriver, *Struct. Bonding*, **1**, 32 (1966).

(2) R. B. King, "Organometallic Syntheses," Vol. 1, Academic Press, New York, N. Y., 1965, p 114.

(3) The adduct like aluminum alkyls is very air sensitive and must be handled under inert atmosphere or vacuum.

Molecular weight and infrared data indicate significant dissociation of the adduct in solution. For the most concentrated solution studied (nominal  $9.2 \times 10^{-3} M$ ) the molecular weight is 505 as determined cryoscopically in benzene (calcd 582). In the presence of excess triethylaluminum infrared absorptions are found at 2044 s, 2004, 2009 (doublet) vs, and 1682 vs  $\text{cm}^{-1}$  in heptane solution. These represent an increase of *ca.* 40  $\text{cm}^{-1}$  for terminal CO stretching frequencies and a decrease of 112  $\text{cm}^{-1}$  from the bridging CO stretching frequency of the parent iron complex.<sup>4</sup> The latter decrease suggests coordination to the oxygen of the bridging carbonyl since similar frequency shifts are found upon the coordination of ketones to Lewis acids.<sup>5</sup>

Coordination of  $\text{Al}(\text{C}_2\text{H}_5)_3$  to the bridging carbonyls is clearly demonstrated by single-crystal X-ray diffraction. Preliminary Weissenberg and precession photographs show monoclinic symmetry and cell constants  $a = 14.45$  (2),  $b = 14.19$  (2),  $c = 14.70$  (3) Å, and  $\beta = 100^\circ 50$  (15)'. Systematic absences of  $hkl$ ,  $h + k \neq 2n$ , and  $h0l$ ,  $l \neq 2n$ , are consistent with space group C2/c or Cc; the observed density of 1.31  $\text{g cm}^{-3}$  (by helium displacement) indicates four molecules per unit cell ( $\rho_{\text{calcd}} = 1.31 \text{ g cm}^{-3}$ ). As described below, the correct space group is C2/c for which the molecule must contain a twofold axis, whereas for Cc no symmetry needs to be imposed on the molecule.

A crystal of approximately cubic dimensions was mounted along its  $[\bar{1}\bar{1}0]$  axis and six layers of integrated equiinclination Weissenberg photographs were taken at room temperature using Mo  $K\alpha$  radiation. Intensities of the reflections were estimated visually and were corrected for Lorentz and polarization effects but not absorption (linear absorption coefficient for Mo  $K\alpha$  is 11  $\text{cm}^{-1}$ ). The data were inter-scaled by comparison of common reflections to yield structural amplitudes for 815 reflections.

The Patterson function clearly indicates the centrosymmetric space group, and therefore the molecule has twofold symmetry. After two least-squares cycles using the trial coordinates, a difference Fourier map gave the positions of the remaining nonhydrogen atoms. At the present state of refinement with all atoms having isotropic temperature factors and without including hydrogen atoms  $R_1 = \Sigma(|F_o| - |F_c|)/\Sigma|F_o| = 0.12$ , and  $R_2 = (\Sigma w(|F_o| - |F_c|)^2/\Sigma wF^2)^{1/2} = 0.13$ . ( $|F_o|$  and  $|F_c|$  are observed and calculated structure amplitudes, respectively, and  $w = 256/F_o^2$  for  $I > 16$  and  $w = I^2/F_o^2$  for  $I \leq 16$  where  $I$  is the raw intensity.)

The crystal structure is composed of discrete monomeric molecular units (Figure 1). The iron-iron distance of 2.49 (1) Å is identical with that of the parent compound.<sup>6</sup> However, in contrast to the solid parent the terminal groups are in a *cis* configuration. Of greatest interest is the coordination of Al to oxygen of the bridging carbonyl. The Al-O distance is 2.00 (2) Å and the C-O-Al angle is 155 (2)°.

A similar adduct  $\text{Fe}_4(\pi\text{-C}_5\text{H}_5)_4(\text{CO})_4 \cdot 4\text{Al}(\text{C}_2\text{H}_5)_3$  may be synthesized from  $\text{Fe}_4(\pi\text{-C}_5\text{H}_5)_4(\text{CO})_4$ <sup>7</sup> and  $\text{Al}(\text{C}_2\text{H}_5)_3$ .

(4) (a) K. Noack, *J. Inorg. Nucl. Chem.*, **25**, 1383 (1963); (b) F. A. Cotton and G. Yagupsky, *Inorg. Chem.*, **6**, 15 (1967).

(5) I. Lindquist, "Inorganic Adduct Molecules of Oxo-Compounds," Academic Press, New York, N. Y., 1963, p 11.

(6) O. S. Mills, *Acta Cryst.*, **11**, 620 (1958).

(7) R. B. King, *Inorg. Chem.*, **5**, 2227 (1966). The structure consists