

# Electron Spin Resonance Study of Heterocycles.

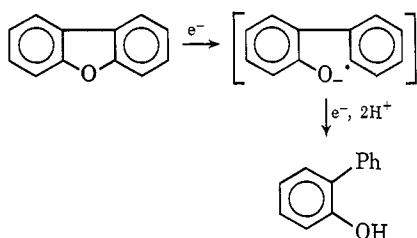
## III. Furan, Isoxazole, and Oxazole Anion Radicals

Paul H. Kasai\* and D. McLeod, Jr.

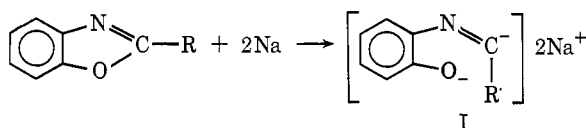
Contribution from the Union Carbide Corporation, Tarrytown Technical Center, Tarrytown, New York 10591. Received February 26, 1973

**Abstract:** Anion radicals of furan, isoxazole, and oxazole were generated in argon matrices, and their esr spectra were examined. In each case, the radical was found to possess a structure resulting from a rupture of an oxygen bond. The negative charge is thus localized on the oxygen atom at one end of the bent chain, while the spin density is localized in the "broken"  $\sigma$  orbital of the atom at the other end.

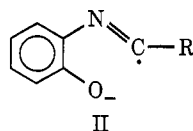
When furans fused to benzo groups or their azole analogs are reduced by alkali metals (e.g., Na in  $\text{NH}_3$ ), the major reaction products are often those involving a rupture of the heterocyclic ring. Evans, *et al.*, for example, reported the formation of 2-hydroxybiphenyl from the reaction between dibenzofuran and sodium in tetrahydrofuran and proposed the following mechanism.<sup>1</sup>



Similarly Knowles and Watt studied the reduction of benzoxazole by Na in liquid ammonia and found the formation of the unstable salt I.<sup>2</sup> This reaction



also suggests the existence of an anion radical intermediate possessing the ring-ruptured structure II.



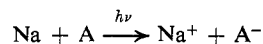
The primary cause for the observed rupture of the heterocyclic ring is undoubtedly the large electronegativity of the oxygen atom. The electrophilic nature of the  $\pi$ -electron system of the benzo group could also contribute to the stability of the ruptured structure.

We decided to investigate the structures of the anion radicals of the basic five-membered heterocyclic system containing an oxygen atom and to examine the effect of its electronegativity upon the structure, free from the effect of any condensed group. The molecules investigated are furan, isoxazole, and oxazole. The electron spin resonance (esr) spectra of the anions of all of these molecules generated within argon matrices at  $\sim 4^\circ\text{K}$  clearly showed that the radicals possess a

ring-ruptured structure. The esr of benzoxazole anion was also examined. The spectrum confirmed the structure II suggested above.

### Experimental Section

Detailed descriptions of the apparatus and the method which would permit generation of charged species within a rare-gas matrix at  $\sim 4^\circ\text{K}$  and the observation of the esr spectrum of the resulting ion radicals have been reported previously.<sup>3</sup> In the present series of experiments, the parent molecules (electron acceptors) were trapped with Na atoms (electron donors) within an argon matrix, the composition being roughly 1000:10:1 for argon atoms, the parent molecules, and Na atoms, respectively. The esr spectrum of the resulting matrix was then examined prior to and after the irradiation of the matrix with "yellow" light ( $\lambda > 5500 \text{ \AA}$ ). Prior to the irradiation, the matrix exhibited only the esr signals due to Na atoms. The irradiation resulted in the disappearance of the Na signals and the appearance of a signal consisting of several hyperfine components centered about the position corresponding to  $g = 2.00$ . The photoinduced signals are assigned to the anion radicals produced by the photoelectron transfer process.



All the esr spectra were obtained while the matrix was maintained at  $\sim 4^\circ\text{K}$ . The frequency of the spectrometer locked to the loaded sample cavity was 9,430 GHz.

Furan, isoxazole, and benzoxazole were obtained from Aldrich Chemical Company, Inc., and were purified by distillation or sublimation prior to matrix deposition. Oxazole was synthesized following the procedure of Brederick and Bangert.<sup>4</sup> The product, oxazole, was identified with its infrared spectrum<sup>5</sup> and the proton nmr spectrum.<sup>6</sup>

### Spectra and Assignments

**Furan.** Figure 1 shows the photoinduced spectrum obtained from an argon matrix containing furan and Na. The doublet-of-doublet pattern of the spectrum is quite discernible. The most extraordinary feature of this spectrum is the magnitude of the larger doublet spacing. A coupling constant of 61 G to a proton is much too large to be expected for a planar  $\pi$  radical. The spectrum, therefore, cannot be assigned to a  $\pi$ -type anion radical retaining the original structure of furan. The spectrum is assigned to the radicals possessing a ring-ruptured structure III. In this structure, the negative charge of the anion is localized on oxygen, and the spin density is localized in the nonbonding  $\sigma$  orbital of the  $\alpha$  carbon. Thus the observed splittings of 17 and 61 G are assigned respectively to the  $\alpha$  and  $\beta$  protons of the open structure as indicated. The

(3) P. H. Kasai, *Accounts Chem. Res.*, **4**, 329 (1971).

(4) H. Brederick and R. Bangert, *Chem. Ber.*, **97**, 1414 (1964).

(1) A. G. Evans, P. B. Roberts, and B. J. Tabner, *J. Chem. Soc. B*, 269 (1966).

(2) C. M. Knowles and G. W. Watt, *J. Org. Chem.*, **7**, 56 (1942).

(5) E. Borello, A. Zecchina, and A. Appiano, *Spectrochim. Acta*, **22**, 977 (1966).

(6) D. J. Brown and P. B. Ghosh, *J. Chem. Soc. B*, 270 (1969).

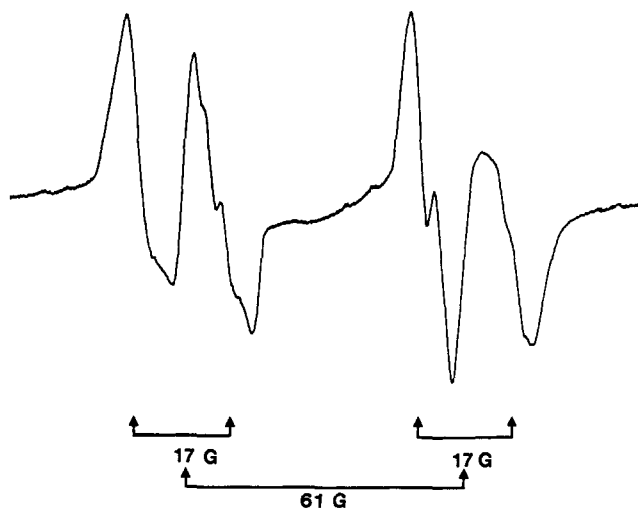


Figure 1. An esr spectrum photoinduced in an argon matrix containing Na and furan.

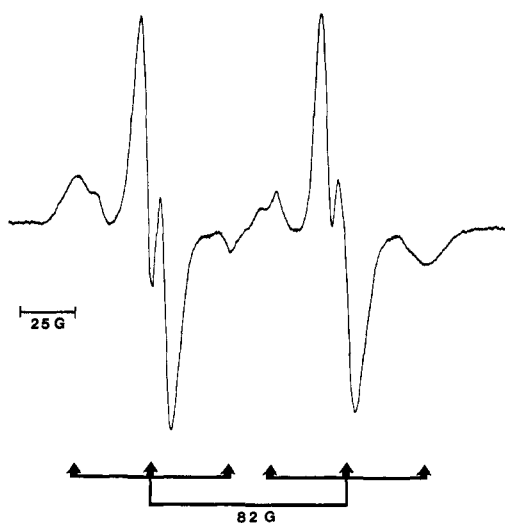
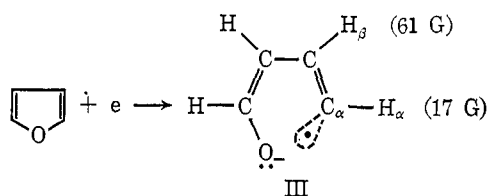
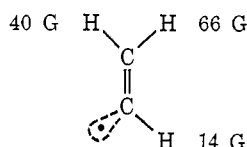


Figure 2. An esr spectrum photoinduced in an argon matrix containing Na and isoxazole.



structure III is essentially a substituted vinyl radical. The known isotropic coupling constants of vinyl radicals are<sup>7</sup>



The proximity of the observed coupling constants of radical III to those of the corresponding protons in vinyl radicals is a further substantiation of the proposed structure and the assignment.

The broadness of the signal and the difference in

(7) P. H. Kasai, *J. Amer. Chem. Soc.*, **94**, 5950 (1972).

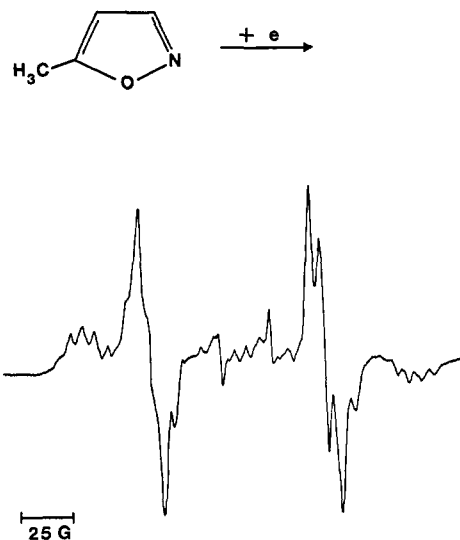
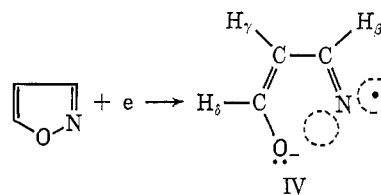


Figure 3. An esr spectrum photoinduced in an argon matrix containing Na and 5-methylisoxazole.

line shape among the quadruplet components are caused by the anisotropies of the  $g$  values, the hyperfine coupling tensors, and the noncoincidence of their principal axes. A closer examination of Figure 1 reveals, however, that some of the components possess further structure indicating small but finite hyperfine interaction with the remaining two protons. The coupling constants to these protons were assessed to be approximately  $3 \pm 1$  G.

**Isoxazole.** The spectrum photoinduced in an argon matrix containing Na and isoxazole is shown in Figure 2. As indicated in the figure, the major pattern of the spectrum can be described as a doublet-of-triplets. The large, isotropic doublet spacing of 82 G is again too large to be attributed to a proton of a  $\pi$ -type anion radical possessing the original planar structure of isoxazole. The triplet feature is due to the  $^{14}\text{N}$  nucleus, and the unique anisotropy ( $A_{\parallel} \gg A_{\perp} \cong 0$ ) of this hfs indicates that the semifilled orbital involves only a  $p_{\pi}$  orbital of the nitrogen and not its  $2s$  orbital.<sup>8</sup> The spectrum, therefore, is assigned to the radical possessing a ring-ruptured structure IV. In this structure,



the negative charge of the anion is again localized on oxygen, and the spin density is localized in the non-bonding  $2p_{\pi}$  orbital of nitrogen. The assigned parameters for the radical IV are

$$A_{\text{iso}}(\text{H}_{\beta}) = 82 \pm 2 \text{ G}$$

$$A_{\parallel}({}^{14}\text{N}) = 35 \pm 2 \text{ G}$$

(8) Examples of radicals possessing this type of hyperfine coupling tensor to  $^{14}\text{N}$  are: NO, J. H. Lunsford, *J. Chem. Phys.*, **46**, 4347 (1967);  $\text{NF}_2$ , P. H. Kasai and E. B. Whipple, *Mol. Phys.*, **9**, 497 (1965);  $\text{H}_2\text{C}=\text{N}$ , ref 9; and anilino radical  $\text{C}_6\text{H}_5\text{NH}$ , P. H. Kasai and D. McLeod, Jr., unpublished results.

(9) E. L. Cochran, F. J. Adrian, and V. A. Bowers, *J. Chem. Phys.*, **36**, 1938 (1962).

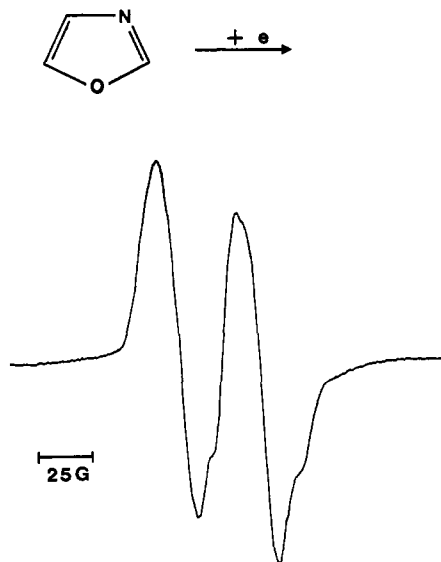


Figure 4. An esr spectrum photoinduced in an argon matrix containing Na and oxazole.

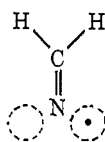
$$A_{\perp}(^{14}\text{N}) = 0 \pm 3 \text{ G}$$

$$g_{\parallel} = 2.002 \pm 0.0005$$

$$g_{\perp} = 2.004 \pm 0.0005$$

The spectrum in Figure 2 also indicates the presence of an additional hyperfine interaction of  $\sim 7$  G to one of the remaining protons. In order to identify the proton responsible for this coupling, the experiment was repeated using 5-methylisoxazole. The resultant spectrum (Figure 3) shows a quartet pattern ( $A \cong 6$  G) expected from the hyperfine interaction with the methyl group in place of the doublet noted above.  $\text{H}_\beta$  thus appears to be responsible for the doublet structure of  $\sim 7$  G.

The radical IV is essentially a substituted methylene imino radical  $\text{H}_2\text{C}=\dot{\text{N}}$ . The hyperfine coupling tensors reported for this radical are



$$A_{\text{iso}}(\text{H}_\beta) = 87.4 \text{ G}$$

$$A_{\parallel}(^{14}\text{N}) = 34.4 \text{ G}$$

$$A_{\perp}(^{14}\text{N}) \cong 0 \pm 4 \text{ G}$$

The proximities of these tensors to those of the corresponding nuclei of the radical IV are a strong substantiation to the proposed structure and the assignment.

**Oxazole.** The spectrum photoinduced in an argon matrix containing Na and oxazole is shown in Figure 4. The simple doublet pattern with a spacing of 35 G observed here can hardly be expected from a  $\pi$ -type anion radical retaining the structure of neutral oxazole. Accordingly the spectrum is assigned to the radical V produced by a ring-rupture process. The negative charge of the anion is again localized on oxygen, while the spin density is localized in the non-bonding  $\sigma$  orbital of the  $\alpha$  carbon. The doublet spac-

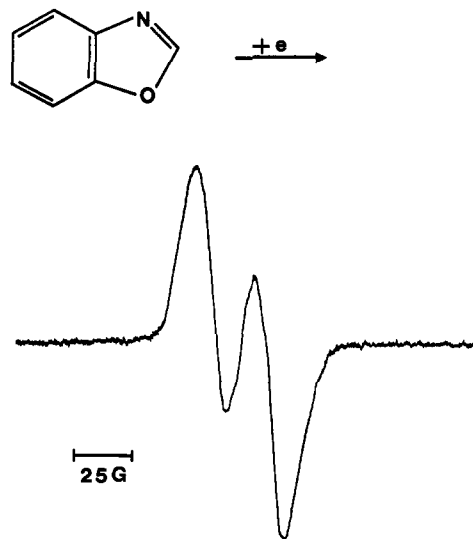
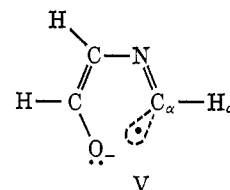


Figure 5. An esr spectrum photoinduced in an argon matrix containing Na and benzoxazole.



ing of 35 G is ascribed to the coupling to the  $\alpha$  proton. The magnitude of this coupling is significantly larger than that known for the methyl radical, or that of the  $\alpha$  proton in the vinyl radical.<sup>7</sup> It has been shown that, for the vinyl radical, the  $\text{C}_\beta=\text{C}_\alpha-\text{H}_\alpha$  section is bent as indicated in the earlier discussion, and the sign of the coupling constant to the  $\alpha$  proton is positive.<sup>7,10-13</sup> The larger coupling constant of oxazole anion radical V must result from a larger angle of bend for the  $\text{N}=\text{C}_\alpha-\text{H}_\alpha$  part, and hence its sign must also be positive.

**Benzoxazole.** Figure 5 shows the spectrum photoinduced in an argon matrix containing Na and benzoxazole. The simple doublet pattern with a spacing of 26 G is quite discernible, but is difficult to interpret in terms of a  $\pi$ -type anion radical possessing the original structure. It is assigned to the radical II proposed earlier. The essential feature of the radical is identical with that of the ring-ruptured oxazole anion V. As expected, the doublet due to II appears slightly sharper than that of V. An interesting aspect is that the fusion of the benzene ring at carbons 4 and 5 of oxazole manifests itself in a smaller coupling constant to the  $\alpha$  proton suggesting a smaller angle of bend for the  $\text{N}=\text{C}_\alpha-\text{H}_\alpha$  section.

## Discussion

In order to obtain further substantiation the assignments proposed in the preceding section, the isotropic coupling constants were calculated for the radicals III, IV, and V using an INDO molecular or-

(10) E. L. Cochran, F. J. Adrian, and V. A. Bowers, *J. Chem. Phys.* **40**, 213 (1964).

(11) F. J. Adrian and M. Karplus, *ibid.*, **41**, 56 (1964).

(12) W. T. Dixon, *Mol. Phys.*, **9**, 201 (1965).

(13) N. M. Atherton and A. Hinchliffe, *ibid.*, **12**, 349 (1967).

Table I. The  $g$  Values and the Observed and Calculated Isotropic Hyperfine Coupling Constants to Protons of Radicals III, IV, and V (in G)

Radical <sup>a</sup>	$g$	N	H <sub>α</sub>	H <sub>β</sub>	H <sub>γ</sub>	H <sub>δ</sub>
III						
Obsd	2.002		17 (±1)	61 (±2)	3 (±1)	3 (±1)
Calcd			21.3	71.8	-2.4	3.8
IV						
Obsd	2.003	12 (±2)		82 (±2)	NR <sup>b</sup>	7 (±2)
Calcd		8.9		67.7	2.0	2.9
V						
Obsd	2.003	NR <sup>b</sup>	35 (±2)		NR <sup>b</sup>	NR <sup>b</sup>
Calcd		-0.4	39.4		-2.8	7.3

<sup>a</sup> For the calculation of radicals III and V, the angle of bend  $\theta$  (see Figure 6) was assumed to be 50°. <sup>b</sup> NR = not resolved.

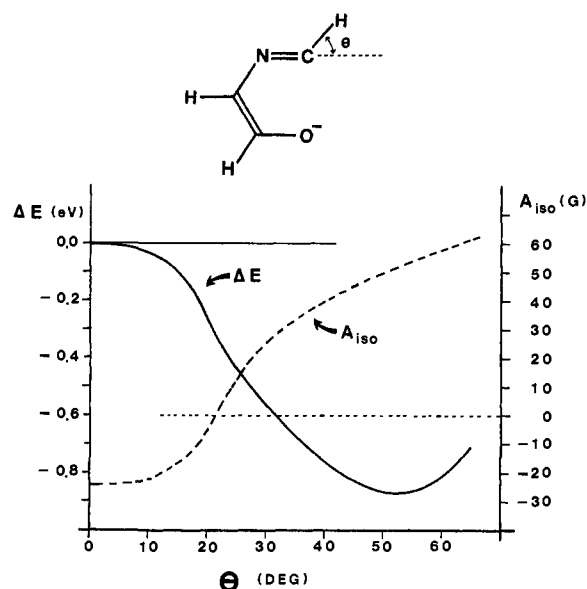


Figure 6. Calculated dependencies of the total energy and the  $\alpha$ -proton coupling constant of oxazole anion V upon the angle of bend at  $N=C_{\alpha}-H_{\alpha}$ .

orbital method.<sup>14</sup> The standard bond lengths and angles given in ref 14 were used for the calculation. The calculated coupling constants are compared with the experimentally determined values (Table I). The agreement between the observed and calculated values can be considered excellent in view of the uncertainties involved in the assumed structures.

The structure of ring-ruptured oxazole anion radical V poses an interesting question regarding the hybridization of the  $\alpha$  carbon. In vinyl radical, which has a bent  $C_{\beta}=C_{\alpha}-H_{\alpha}$  structure, the bending does not affect the  $\pi$  system, but lowers the energy of the half-occupied orbital at the expense of  $s$  character of the  $C_{\alpha}$   $\sigma$  orbital in the  $C=C$  bond. When a nitrogen is substituted at the  $\beta$  position, a decrease in the  $s$  character of the  $C_{\alpha}$   $\sigma$  orbital increases the electronegativity difference between  $C_{\alpha}$  and N, thereby strengthening the  $C=N$  bond. One would thus predict a greater deviation of the  $C_{\alpha}$  hybridization from a linear  $sp$  type toward a bent  $sp^2$  for the case of radical V. Shown in Figure 6 are the dependencies of the total energy and the isotropic coupling constant to the  $\alpha$  proton of the radical V upon the angle of bend  $\theta$  calculated by an

(14) J. A. Pople and D. L. Beveridge, "Approximate Molecular Orbital Theory," McGraw-Hill, New York, N. Y., 1970. The calculations were performed utilizing an INDO program obtained from the Quantum Chemistry Program Exchange, Indiana University.

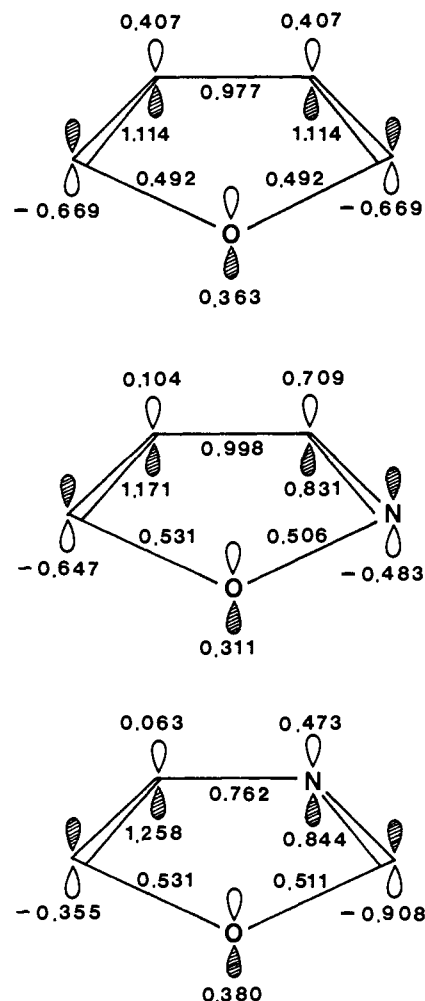


Figure 7. The overlap populations between the neighboring first row atoms of furan, isoxazole, and oxazole anions in their cyclic forms (numeral given inside each ring) and the coefficients of the LCAO descriptions of the semifilled  $\pi$ -type molecular orbitals of these anion radicals (numerals given outside each ring).

INDO molecular orbital method. The figure clearly shows the energy minimum at  $\theta \cong 50^\circ$ , indicating stability for a bent structure. The  $\alpha$  proton coupling constant, which is  $-24$  G at  $\theta \cong 0^\circ$ , increases to  $+50$  G at  $\theta \cong 50^\circ$ . A similar calculation performed for the vinyl radical<sup>7</sup> showed the energy minimum at  $\theta \cong 30^\circ$ . These theoretical results strongly support our assertion that the sign of the  $\alpha$ -proton coupling constant of oxazole anion radical V is positive and its  $N=C_{\alpha}-H_{\alpha}$  part has a larger angle of bend than the corresponding part of the vinyl radical or furan anion radical III.

Depicted in Figure 7 are the total overlap populations between the neighboring first row atoms of furan, isoxazole, and oxazole anions in their "cyclic states" calculated by an EHT molecular orbital method.<sup>15</sup> Depicted also in the figure are the LCAO descriptions of the semifilled molecular orbitals of these anions. It is immediately clear that, in each case, the orbital into which the extra electron enters possesses a strong antibonding character across the oxygen bonds, and the ring rupture of the anion occurs at the weakest bond. It should be pointed out that the bonds involving the

(15) R. Hoffmann, *J. Chem. Phys.*, **39**, 1307 (1963).

oxygen atom are the weakest bonds in the neutral state also. The additional electron of the anion makes them even weaker. Most interestingly, in the case of neutral oxazole, the calculation showed that the C<sub>5</sub>-O bond is weaker than the C<sub>2</sub>-O bond. As shown in the figure, the situation is reversed for the anion, predicting correctly the bond to be ruptured.

The ring-rupture processes observed in the present series of heterocycles thus can be understood as a manifestation of the electronegativity of oxygen and the weakness of the oxygen bonds, particularly in their anionic state.

## Relation between Rate and Equilibrium Constants for Proton-Transfer Reactions<sup>1a</sup>

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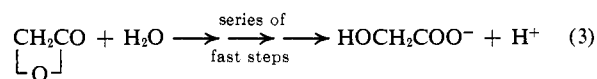
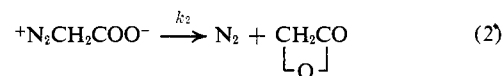
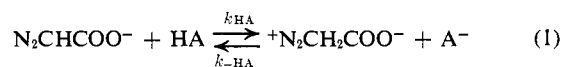
*Contribution from the Department of Chemistry, University of Minnesota, Minneapolis, Minnesota 55455. Received January 10, 1973*

**Abstract:** Considerable curvature is found in the Brønsted plot for the hydrolysis of diazoacetate ion by trialkylammonium salts. This curvature can be accounted for by Marcus' theory of atom transfer. The resultant parameters serve to separate from the free energy of activation that part which must be provided before the rate-determining proton transfer can take place and is, consequently, insensitive to the spontaneity of the overall reaction. The variation of the primary hydrogen isotope effect with structure in the same reactions is successfully correlated by the same parameters. A number of other reactions, for which data are taken from the literature, seem to follow similar patterns.

In the next few years it seems likely that the notion of a complete reaction mechanism will change from a series of equations identifying the starting state, the transition state, and any intermediates to a more or less complete description of the atomic motions leading from starting state to transition state and the potential energy hypersurface over which they occur.<sup>2</sup> There is presently no heterolytic, condensed phase, reaction for which such a complete mechanism can be said to be known, although such reactions are the subject of most current chemical and biochemical study. This lack can be traced to the fact that such reactions involve the repositioning and rebonding of large numbers of atoms (including those of solvent molecules). To many it has long seemed likely that the simplest of such reactions would be proton-transfer reactions.<sup>3</sup> Among those it seems likely that the most readily understood will be homogeneous series in which those members which are strongly spontaneous reach large rate constants ( $10^4$ – $10^8$   $M^{-1} \text{sec}^{-1}$ ) but do not become diffusion limited. The reason for that choice is that systematic changes in  $\Delta F^\circ$  of reaction can then be achieved which are of the order of the free energy of activation itself. Such changes should change the transition-state structure, as shown by changes in structure-reactivity re-

lationships (Hammett or Brønsted parameters) and isotope effects. From the sensitivity of the transition-state structure to changes in  $\Delta F^\circ$ , information about the original transition-state structure can be obtained.

General acid-catalyzed diazoacetate hydrolysis is a reaction of the desired type.<sup>4</sup> The rate-determining proton transfer (eq 1) is followed by fast, irreversible steps (eq 2 and 3) which permit the reaction to be monitored by conventional techniques.



(The  $k$ 's are rate constants and follow previously established conventions.) When HA is  $\text{H}^+(\text{aq})$   $k_{HA}$  has a value of  $6.5 \times 10^4$   $M^{-1} \text{sec}^{-1}$ .

We have previously reported<sup>5</sup> that phenols and carboxylic acids generate quite different Brønsted  $\alpha$ 's<sup>6</sup> when used as catalysts for this reaction, but that the two sets of data combined generate a continuous curve of the

(1) (a) Supported, in part, by the National Science Foundation through Grants GP-7915, GP-13172, and GP-31360X. (b) Du Pont Summer Fellow, 1969; Mobil Oil Summer Fellow, 1970; Lubrizol Fellow, 1970–1971.

(2) L. Salem, *Accounts Chem. Res.*, **4**, 322 (1971).

(3) R. P. Bell, "Acid-Base Catalysis," Clarendon Press, Oxford, 1941, Chapter VIII.

(4) M. M. Kreevoy and D. E. Konasewich, *J. Phys. Chem.*, **74**, 4464 (1970).

(5) M. M. Kreevoy and D. E. Konasewich, *Advan. Chem. Phys.*, **21**, 241 (1972).

(6) J. N. Brønsted, *Chem. Rev.*, **5**, 231 (1928).