yields 20 × 10^5 $l.^2/(mol^2\ sec)$ for the overall rate constant for HI production at 633°K, whereas Sullivan measures 9.38 × 10^5 $l.^2/(mol^2\ sec)$.[7]

Thus, the present investigations give a detailed explanation for Sullivan's experimental observation that the molecular mechanism is forbidden, but that an atomic mechanism is allowed, as had previously been suggested by Semenov[14] and by Eyring.[15] Noyes' suggestion[16] that (1) might be forbidden as a result of the trajectory restrictions imposed by the dynamic effect of momentum conservation is essentially confirmed. A detailed report is in preparation.

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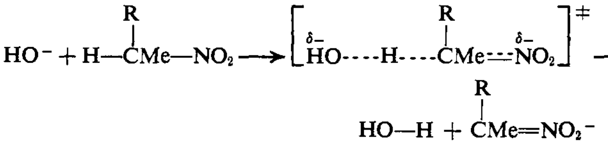
Deviant Brønsted Relations[1]

Sir:

The exponent α of the Brønsted relation is generally thought to measure the position of the transition state along the reaction coordinate of a proton-transfer process.[2] It is a necessary consequence of this view that α should lie between the limits zero and unity, and yet Brønsted relations with exponents greater than 1 and less than 0 have recently been reported.[3] I wish to show how these unusual Brønsted relations may be understood on a molecular level and to point out some implications of this on the use of Brønsted exponents as measures of transition-state structure.[4]

It is easily demonstrated that the Brønsted relation correlates rate constants of a proton-transfer reaction with equilibrium constants for the same process and that the Brønsted exponent is equal to the substituent effect on $\Delta F^{\ddagger}$ divided by the substituent effect on $\Delta F°$; in the symbolism of ref 2, $\alpha = \delta_R\Delta F^{\ddagger}/\delta_R\Delta F°$. It follows then that a Brønsted exponent greater than unity indicates a reaction in which the substituent effect on $\Delta F^{\ddagger}$ is greater than the substituent effect on $\Delta F°$. However such a situation goes against the notion that structural changes occurring during a chemical reaction take place continuously as the initial state changes into the final state and that the interaction of a substituent with such a system must also change continuously between initial- and final-state limits and must not pass through extrema outside these limits. It is possible, however, to retain the essential features of this idea and still permit $\delta_R\Delta F^{\ddagger}$ to exceed $\delta_R\Delta F°$ by recognizing that new interactions, absent from initial or final states, can be present in transition states. Such new interactions exist, for example, in the transition state of every bimolecular proton transfer reaction: union of the reactants creates forces not present before the reacting molecules come together or after they separate.

Consider the process for which α was recently found to be equal to 1.4: reaction of substituted nitroalkanes with hydroxide ion (eq 1).[3] The effect of the substituent R on $\Delta F°$ for this reaction, $\delta_R\Delta F°$, may be assigned to the electrical interaction of R with a negatively charged nitro group in the final state, I_{R,NO_2^-}; *i.e.*, $\delta_R\Delta F° = I_{R,NO_2^-}$. There will be a corresponding interaction in the transition state whose magnitude depends on the fraction of an electronic charge transferred from the hydroxide ion, x; *i.e.*, this contribution to $\delta_R\Delta F^{\ddagger}$ will be equal to xI_{R,NO_2^-}. In addition, there will be another effect in the transition state contributing to $\delta_R\Delta F^{\ddagger}$: the interaction of R with the partly charged hydroxide ion; this effect will be equal to $(1 - x)\cdot I_{R,HO^-}$, where I_{R,HO^-} is the interaction of R with a fully charged hydroxide ion situated in its transition-state position. Since this hydroxide ion is remote from R in the initial state, and since it no longer exists in the final state, the initial- and final-state limits of this effect will be zero. Thus, this is a transition-state interaction which is absent from initial and final states.



$$HO^- + H\text{—}\overset{\overset{R}{|}}{C}Me\text{—}NO_2 \longrightarrow \left[\overset{\delta-}{HO}\cdots H\cdots\overset{\overset{R}{|}}{C}Me\text{≕}\overset{\delta-}{NO_2}\right]^{\ddagger} \longrightarrow HO\text{—}H + \overset{\overset{R}{|}}{C}Me\text{=}NO_2^- \quad (1)$$

This model leads directly to values of α greater than unity whenever the substituent interacts more strongly with a fully charged hydroxide ion than with a fully charged nitro group; *i.e.*, $\alpha = [xI_{R,NO_2^-} + (1 - x)\cdot I_{R,HO^-}]/I_{R,NO_2^-}$ is greater than 1 when $I_{R,HO^-} > I_{R,NO_2^-}$. This is likely to be the case in the present reaction, for geometrical considerations show that the distances between R and the centers of negative charge in the hydroxide ion and the nitro group will be comparable at the transition state, but the effective dielectric constant in the direction of the nitro group should exceed that in the direction of the hydroxide ion.

Deviant behavior in the series nitromethane, nitroethane, and 2-nitropropane can also be explained in a similar way. The acidity of these substances increases in the order given,[5] but their rates of reaction with hydroxide ion decrease in the same sequence;[6] combination of these two sets of data gives $\alpha = -0.7$.[3] The methyl groups successively introduced along this series will decrease acidity through their inductive effect but raise acidity by hyperconjugative stabilization of the nitronate ion (**1**). The latter effect predominates as it usually does in electron release to a positive center; this makes $\delta_R\Delta F°$ negative. Both of these interactions will be only partly realized at the transition state, but their sum will nevertheless still amount to net stabi-

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[1] This research was supported by a grant (GP 9253) from the National Science Foundation to the Illinois Institute of Technology.

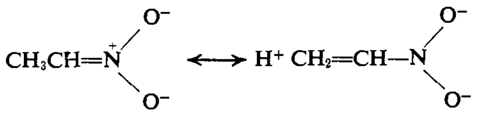
[2] See, for example, J. E. Leffler and E. Grunwald, "Rates and Equilibria of Organic Reactions," Wiley, New York, N. Y., 1963, p 235.

[3] F. G. Bordwell, W. J. Boyle, Jr., J. A. Hautala, and K. C. Yee, *J. Amer. Chem. Soc.*, **91**, 4002 (1969).

[4] For a discussion of this along somewhat different lines, see R. A. Marcus, *ibid.*, **91**, 7224 (1969).

[5] D. Turnbull and S. Maron, *ibid.*, **65**, 212 (1943); G. W. Wheland and J. Farr, *ibid.*, **65**, 1433 (1943).

[6] R. P. Bell and D. M. Goodall, *Proc. Roy. Soc., Ser. A*, **294**, 273 (1966).



$$\mathrm{CH_3CH{=}\overset{+}{N}(O^-)_2 \longleftrightarrow H^+\ CH_2{=}CH{-}N(O^-)_2}$$

1

lization by methyl groups, as in the final state. Superimposed on this will be the transition-state interaction of hydroxide ion with methyl groups which is destabilizing (inductive effect). As long as this destabilizing interaction (positive contribution to $\delta_R\Delta F^{\ddagger}$) exceeds the difference between the inductive and hyperconjugative interactions of the methyl and nitro groups in the transition state, $\delta_R\Delta F^{\ddagger}$ will be positive; since $\delta_R\Delta F^\circ$ is negative, α will be less than zero. Simple electrostatic calculations show that such a balance of effects is in fact reasonable for this system.

Deviant Brønsted relations such as these should be observed whenever the new transition-state interaction, which we shall call the intermolecular effect, exceeds the intramolecular effect of the substituent within the catalyst. This is especially likely to occur with nitroalkanes and other pseudoacids and -bases, which owe their acidity to the presence of groups capable of removing negative charge from the vicinity of the proton transfer site and usually also from the immediate neighborhood of substituents introduced for the purpose of varying acid strength. In more conventional catalysts, such as carboxylic acids, phenols, amine salts, etc., the charge either remains on the atom from which the proton is transferred or else moves nearer the substituent; in these cases, the intermolecular effect will be small compared to the intramolecular effect, and more normal Brønsted exponents will be observed. The intermolecular effect, however, will not be totally absent, and its presence will give α a value different from that of some other measure of the position of the transition state along the reaction coordinate, say x, the fraction of electronic charge transferred. Calculations, which will be reported in full later, show that an intermolecular effect only one-tenth of the intramolecular effect will, at $x = 0.5$, produce a 10% difference between α and x for proton transfer to a neutral or a negatively charged substrate, and the discrepancy will be greater for substrates of different charge types.

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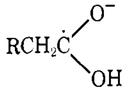
A New Type of Radical in Irradiated Single Crystals of Carboxylic Acids

Sir:

During the past decade extensive studies have been made of the electron spin resonance of irradiated single crystals of carboxylic acids. The radicals found so far may be classified into the following four categories. Irradiation at low temperature gives anion π radicals (I) produced by capture of an ejected electron[1] and neutral π radicals (II) produced by removal of the carboxylic group;[1a,2] while irradiation at room temperature, or elevation of the specimen temperature after irradiation at low temperature, gives a π radical (III) produced by rupture of the hydrogen atom attached to the α carbon of the carboxylic group, in the case of saturated compounds,[3] and π radicals (IV) produced by addition of H or R to the double bond, in the case of unsaturated compounds.[4]



$$\mathrm{RCH_2\dot{C}(O^-)OH}$$

I

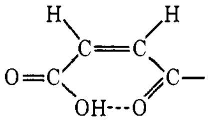
$\mathrm{RCH_2\cdot}$ II

$\mathrm{R\dot{C}HCOOH}$ III

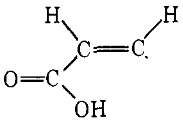
$\mathrm{R'CHX{-}\dot{C}R''COOH}$ IV, X = H or R

Recently we have found a new type of radical which is believed to be a precursor of the radical of type II. The esr spectra of a single crystal of maleic acid irradiated at 77°K show that the anion π radical (C_π) of type I and the new type of radical (O_σ), having a large g anisotropy with a small hyperfine structure, are predominantly produced together with a minor product of the vinyl-type radical (V_σ) which corresponds to type II. O_σ is very unstable and disappears by subsequent exposure to a tungsten light or by warming slightly from 77°K. Instead, the signal due to V_σ was enhanced at the expense of the signal due to this unstable radical. Although both normal maleic acid and the deuterated one (DOOCCH=CHCOOD) were examined, the hyperfine and g tensors determined from the spectra of the latter are listed in Table I, since the hyperfine couplings due to the OH protons have not been analyzed yet.

It was found from comparison with the crystallographic data[5] that the direction of the maximum principal value (2.0261) of the g tensor of O_σ is approximately along the side C–O(H) bond and that of the minimum value (2.0035) is nearly perpendicular to the C–O(H) bond in the molecular plane. From this, together with the large g anisotropy, O_σ is assigned to the carboxyl radical produced by the removal of the OH proton which participates in intermolecular hydrogen bonding. The hyperfine coupling is due to a closer vinylene proton, since the direction of the maximum principal value is along the line connecting the side C–O(H) oxygen and the closer vinylene proton. The magnitude and the anisotropy of the hyperfine tensor are also consistent with this interpretation. Since the half-filled orbital lies in the molecular plane, this radical is a localized σ radical, in contrast to the π radical produced by the removal of the OH proton in



O_σ



V_σ

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