

It should be pointed out that these results contrast with previous results on the photochemistry of the 6-substituted 9-thiabicyclo[3.3.1]non-2-one system. For that case, ring fission followed by internal disproportionation between the radical centers was the preferred route.<sup>17</sup> The presence of a double bond in the 6 position of the thiabicyclic system seems to play an important role in the photochemistry of this ring system. In view of the novelty of the rearrangement and especially because the limited available data suggest that saturated  $\beta$ -keto sulfides react in a different manner, the photochemistry of a variety of unsaturated  $\beta$ -keto sulfides and related compounds is presently under investigation in this laboratory.

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- (17) V. C. Canter and J. F. Moser, *Helv. Chim. Acta*, **51**, 300 (1968).  
 (18) Alfred P. Sloan Foundation Fellow, 1968-1970.

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### Brønsted Coefficients Larger Than 1 and Less than 0 for Proton Removal from Carbon Acids

Sir:

The Brønsted equation is widely applicable to reactions involving general-acid and general-base catalysis.<sup>1</sup> Brønsted correlations also often hold for nucleophilic catalysis<sup>2</sup> and for proton abstractions from carbon acids, including nitroalkanes,<sup>3</sup> ketones,<sup>1,4</sup> sulfones,<sup>5</sup> and hydrocarbons.<sup>6</sup> For reactions involving proton transfers Brønsted coefficients have been generally assumed to be limited to the range of 0 to +1.<sup>7</sup> It is the purpose of this communication to point out that in the nitroalkane series Brønsted relationships with coefficients less than zero and greater than one exist, and to discuss the reasons for these "deviations."

It has been known for some time that an inverse relationship between rates of proton abstraction and acidities exists in the series  $\text{CH}_3\text{NO}_2$ ,  $\text{MeCH}_2\text{NO}_2$ ,  $\text{Me}_2\text{CHNO}_2$ . Here there is a progressive and substantial decrease in the rates of proton abstraction by hydroxide ion (relative rates 113:18:1.0), whereas the acidities change in the opposite manner (relative  $pK_a$ 's: 10.2, 8.5, and 7.7).<sup>8</sup> Similarly, we have found

(1) R. P. Bell, "The Proton in Chemistry," Cornell University Press, Ithaca, N. Y., 1963, Chapter X.

(2) T. C. Bruice and S. J. Benkovic, "Biorganic Mechanisms," Vol. I, W. A. Benjamin, Inc., New York, N. Y., 1966, pp 37-38.

(3) (a) K. J. Pedersen, *Kgl. Danske Vid. Selsk. Math.-fys. Medd.*, **12**, No. 1 (1932); (b) S. H. Maron and V. K. LaMer *J. Am. Chem. Soc.*, **61**, 2018 (1939); (c) R. G. Pearson and F. V. Williams, *ibid.*, **76**, 258 (1954); (d) M. J. Gregory and T. C. Bruice, *ibid.*, **89**, 2327 (1967).

(4) J. A. Feather and V. Gold, *J. Chem. Soc.*, 1752 (1965).

(5) R. H. Imes (unpublished results) has found a Brønsted coefficient of 0.82 from a plot of  $\log k$  for deuterium exchange in methanol vs.  $\log K_a$  in DMSO for the  $\text{ArCH}_2\text{SO}_2\text{CH}_3$  series.

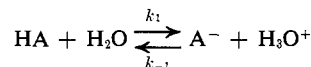
(6) A. Streitwieser, Jr., and J. H. Hammons, *Progr. Phys. Org. Chem.*, **3**, 41 (1965).

(7) (a) K. J. Pedersen, *J. Phys. Chem.*, **38**, 581 (1934); (b) J. E. Leffler and E. Grunwald, "Rates and Equilibria in Organic Reactions," John Wiley & Sons, Inc., New York, N. Y., 1963, pp 156-168, 238-242; (c) M. Eigen, *Angew. Chem. Intern. Ed. Engl.*, **3**, 1 (1964).

(8) D. Turnbull and S. Maron, *J. Am. Chem. Soc.*, **65**, 212 (1943); G. W. Wheland and J. Farr, *ibid.*, **65**, 1433 (1943).

that the rate of proton abstraction by base from nitrocyclobutane is 3.9 times that from nitrocyclopentane in 50% v/v MeOH-H<sub>2</sub>O, despite the fact that the  $pK_a$  of nitrocyclobutane is 1.9 units *higher* than that of nitrocyclopentane in this medium.<sup>9</sup> In such instances a Brønsted plot would give a negative slope. It might be argued, however, that these deviations are caused because the structural variation occurs directly at the acidic site. This objection has now been removed by an investigation of the systems  $\text{ArCHMeNO}_2$  and  $\text{ArCH}_2\text{CHMeNO}_2$ . A plot of  $\log k_1$  for the rates of base-initiated proton abstraction vs.  $\log K_a$ , both in 50% v/v MeOH-H<sub>2</sub>O, revealed for each system a Brønsted coefficient larger than 1. For the  $\text{ArCHMeNO}_2$  system (12 substituents) a Brønsted plot (correlation coefficient = 0.992) gave a slope of 1.31. For the  $\text{ArCH}_2\text{CHMeNO}_2$  system (13 substituents) a Brønsted plot (correlation coefficient = 0.977) gave a slope of 1.61. Since the Brønsted coefficients for the forward and reverse reactions must sum to 1, this means that the Brønsted coefficients for protonation of the  $\text{ArCMeNO}_2^-$  and  $\text{ArCH}_2\text{CMeNO}_2^-$  ions by the solvent (plot of  $\log k_{-1}$  vs.  $\log K_a$ ) must be -0.31 and -0.61, respectively.

$$\log k = \alpha \log K_a + C$$



$$K_a = k_1/k_{-1}$$

The apparent restriction of the values of Brønsted coefficients to the range of 0 to +1 arises from the fact that application of the Brønsted relationship has been limited, hitherto, largely to oxygen acids and bases ( $\text{RCO}_2\text{H}$  and  $\text{RCO}_2^-$ ) or nitrogen acids and bases ( $\text{ArNH}_3^+$  and  $\text{ArNH}_2$  or pyridinium ions and pyridines) where the positions of the equilibria ( $K_a$ ) are more sensitive to structural changes than are the rates ( $k_1$  and  $k_{-1}$ ). This is a consequence of the fact that structural changes in these acids (and their conjugate bases) affect  $k_1$  and  $k_{-1}$  in an *opposite manner*. For example, substitution of an electron-withdrawing substituent (e.g., *m*-NO<sub>2</sub>) for a hydrogen atom of  $\text{PhCO}_2\text{H}$  will increase  $k_1$  and decrease  $k_{-1}$ . For carbon acids, however, the extensive structural reorganization accompanying the formation of the anion can lead to situations in which substituent changes affect  $k_1$  and  $k_{-1}$  in the *same manner*. For example, substitution of an electron-withdrawing group (e.g., *m*-NO<sub>2</sub>) for a hydrogen atom of  $\text{PhCHMeNO}_2$  increases  $k_1$  but also increases  $k_{-1}$ . As a result, the rate of proton removal ( $k_1$ ) by a base, such as hydroxide, is more sensitive to structural changes than is the equilibrium constant (Brønsted coefficient larger than 1). For the reverse reaction ( $k_{-1}$ ) the rate of proton abstraction by  $\text{ArCMeNO}_2^-$  from the solvent will be affected in an inverse manner by substituent effects relative to  $k_1$  or  $K_a$  (negative Brønsted coefficient). For  $\text{ArCMeNO}_2^-$  and  $\text{ArCH}_2\text{CMeNO}_2^-$  this leads to the amusing situation where substitution of a *m*-NO<sub>2</sub> group for hydrogen in the parent nitronate ion causes an *increase* in the basicity of the nitronate ion.

In the series  $\text{CH}_3\text{NO}_2$ ,  $\text{MeCH}_2\text{NO}_2$ ,  $\text{Me}_2\text{CHNO}_2$  proton abstraction by hydroxide ion is retarded by

(9) H. Shechter and coworkers obtained similar results in other media some time ago (H. Shechter, unpublished results privately communicated).

methyl substitution, but proton abstraction by the nitronate ion,  $\text{CH}_2=\text{NO}_2^-$ , from the solvent is retarded to an even greater extent. The result is a negative Brønsted coefficient for a plot of  $\log k_1$  vs.  $\log K_a$  ( $\alpha \cong -0.7$ ) and a coefficient larger than 1 for a plot of  $\log k_{-1}$  vs.  $\log K_b$  ( $\beta \cong 1.7$ ).

Nitroalkanes no doubt represent the extreme among monofunctional carbon acids with respect to a greater sensitivity of rates (of proton transfer) than equilibria to structural change. Brønsted coefficients beyond the 0 to +1 range should be observed, however, with certain other carbon acids of comparable strength and perhaps with some other monofunctional carbon acids where structural reorganization in forming the anion is extensive (e.g., ketones).

It has been suggested that the nearness of the Brønsted coefficient to 0 or +1 can be used as a guide to the position of the transition state along the reaction coordinate,<sup>7b</sup> and this idea has gained considerable acceptance.<sup>3d,10</sup> The present results indicate that this view requires modification, at least for carbon acids.

**Acknowledgment.** This work was supported by the National Science Foundation (GP 7065).

(10) (a) Reference 2b, pp 30-37; (b) J. O. Edwards, "Inorganic Reaction Mechanisms," W. A. Benjamin, Inc., New York, N. Y., 1964, Chapter 3; (c) E. M. Kosower, "Physical Organic Chemistry," John Wiley & Sons, Inc., New York, N. Y., 1968, p 18; (d) R. A. Marcus, *J. Phys. Chem.*, **72**, 891 (1968).

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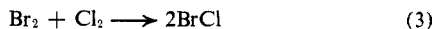
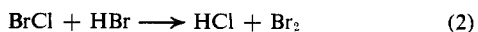
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### The Gas Phase Chlorine Plus Hydrogen Bromide Reaction. A Bimolecular Reaction of Diatomic Molecules

Sir:

The recent work of Sullivan<sup>1</sup> has demonstrated that the reaction  $\text{H}_2 + \text{I}_2 \rightarrow 2\text{HI}$  is not a bimolecular elementary process as previously thought. It is therefore important to determine whether such processes can indeed occur. We have now obtained evidence for bimolecular mechanisms for at least some of the overall reactions.<sup>2</sup>



High purity tank HBr (99.8%) and  $\text{Cl}_2$  (99.5%) in carrier gas consisting of  $\text{N}_2$  (less than 8 ppm  $\text{O}_2$ ) or medical grade air at a flow of 100 cc/sec were mixed in a stopped-flow apparatus with transit time about 0.1 sec similar to that of Johnston.<sup>3</sup> The reaction was monitored with monochromatic light by feeding the output of a photomultiplier tube to an oscilloscope. Numerous runs in a cell with 0.6-cm diameter started with either  $\text{Cl}_2$  or HBr in excess and varied the initial concentration of each constituent over fivefold. Each

(1) J. H. Sullivan, *J. Chem. Phys.*, **46**, 73 (1967).

(2) Preliminary studies were made by W. Jost, *Z. Physik. Chem.*, **B14**, 413 (1931).

(3) H. S. Johnston, *Discussions Faraday Soc.*, **17**, 14 (1954).

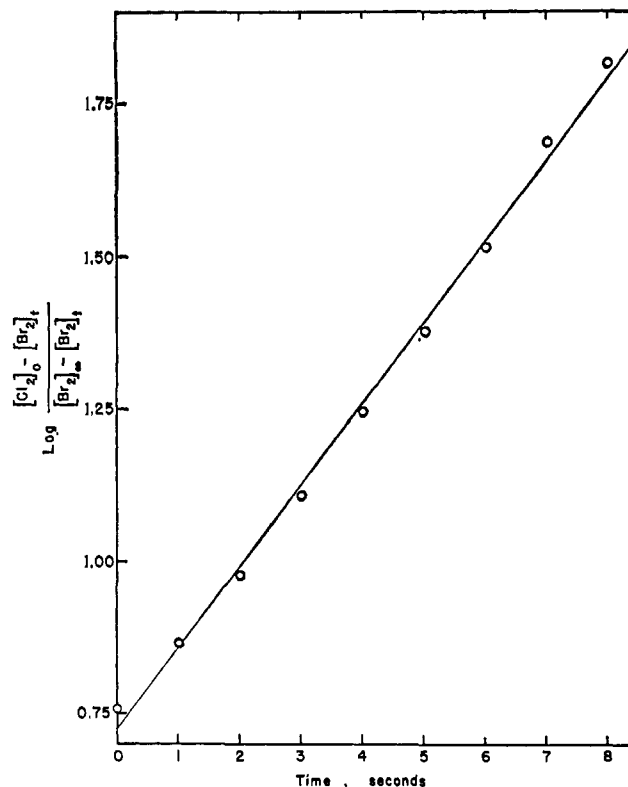


Figure 1. Representative plot of  $\log ([\text{Cl}_2]/[\text{HBr}])$  against time for run with  $[\text{Cl}_2]_0 = 5.76 \times 10^{-3}$  mol/l. and  $[\text{HBr}]_0 = 2.07 \times 10^{-3}$  mol/l. Reaction was followed at 510 nm where only  $\text{Br}_2$  absorbs. Rate constant, obtained by multiplying the slope by  $2.303/(2[\text{Cl}_2]_0 - [\text{HBr}]_0)$ , is 32.7 l./mol sec).

run gave a very satisfactory plot (Figure 1 being a typical example) consistent with the kinetics  $-d[\text{Cl}_2]/dt = d[\text{Br}_2]/dt = k_{\text{ex}}[\text{Cl}_2][\text{HBr}]$  with a mean value of  $k_{\text{ex}} = 30 \pm 5$  l./mol sec at the ambient temperature of 300°K. The same kinetics and rate constant were observed for another set of runs in a cell of diameter 1.8 cm.

Around 370 nm (the isobestic point of  $\text{Cl}_2$  and  $\text{Br}_2$  absorption), no significant variation of optical density was observed during scanning times from 5 msec to 10 sec; therefore no significant concentration of  $\text{BrCl}$  builds up during such times. This observation requires that  $k_2$  is at least 10 to 20 times larger than  $k_1$  and that  $k_3$  is also much smaller than  $k_1$ . For such rate constant ratios, it is a good approximation to set  $k_{\text{ex}} = k_1$ .

For several runs, absorption spectra between 320 and 600 nm were taken at intervals from 5 min up to 20 hr after the reactants were mixed. Hydrogen halides do not absorb in this wavelength region, but halogens do. When HBr was in excess, the spectrum as soon as it could be measured reproduced the published<sup>4</sup> absorption spectrum of  $\text{Br}_2$  and confirmed the equivalence of  $\text{Cl}_2$  consumed and  $\text{Br}_2$  produced. When  $\text{Cl}_2$  was in excess, the spectrum 5-10 min after mixing could be interpreted as a sum of  $\text{Br}_2$  and  $\text{Cl}_2$  spectra, and the behavior between 370 and 410 nm indicated no significant absorption by  $\text{BrCl}$ . During the subsequent 40 min, the concentrations of  $\text{Br}_2$  and  $\text{Cl}_2$  decreased strongly, and an equivalent increase in  $\text{BrCl}$  was observed. After several hours, the constant spectrum attained could be interpreted quantitatively in terms of

(4) D. J. Seery and D. Britton, *J. Phys. Chem.*, **68**, 2263 (1964).