methyl substitution, but proton abstraction by the nitronate ion, $CH_2{=}NO_2^-$, 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,[7b] and this idea has gained considerable acceptance.[3d,10] 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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The Gas Phase Chlorine Plus Hydrogen Bromide Reaction. A Bimolecular Reaction of Diatomic Molecules

Sir:

The recent work of Sullivan[1] has demonstrated that the reaction $H_2 + I_2 \rightarrow 2HI$ 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.[2]

$$Cl_2 + HBr \longrightarrow HCl + BrCl \quad (1)$$

$$BrCl + HBr \longrightarrow HCl + Br_2 \quad (2)$$

$$Br_2 + Cl_2 \longrightarrow 2BrCl \quad (3)$$

High purity tank HBr (99.8%) and Cl_2 (99.5%) in carrier gas consisting of N_2 (less than 8 ppm 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.[3] 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 Cl_2 or HBr in excess and varied the initial concentration of each constituent over fivefold. Each run gave a very satisfactory plot (Figure 1 being a typical example) consistent with the kinetics $-d[Cl_2]/dt = d[Br_2]/dt = k_{ex}[Cl_2][HBr]$ with a mean value of $k_{ex} = 30 \pm 5$ 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.

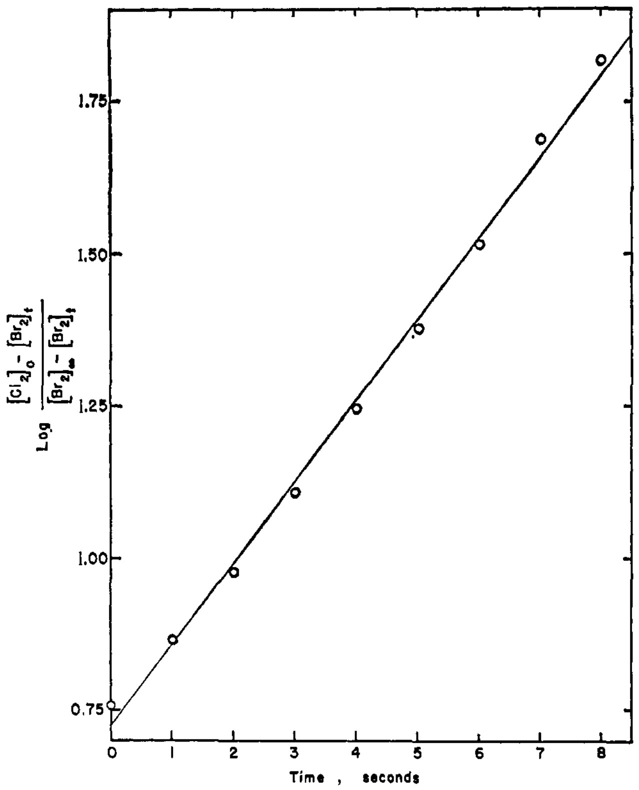

Figure 1. Representative plot of log ($[Cl_2]/[HBr]$) against time for run with $[Cl_2]_0 = 5.76 \times 10^{-3}$ mol/l. and $[HBr]_0 = 2.07 \times 10^{-3}$ mol/l. Reaction was followed at 510 nm where only Br_2 absorbs. Rate constant, obtained by multiplying the slope by $2.303/(2[Cl_2]_0 - [HBr]_0)$, is 32.7 l./mol sec).

Around 370 nm (the isobestic point of Cl_2 and 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 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 $k_{ex} = k_1$.

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[4] absorption spectrum of Br_2 and confirmed the equivalence of Cl_2 consumed and Br_2 produced. When Cl_2 was in excess, the spectrum 5–10 min after mixing could be interpreted as a sum of Br_2 and Cl_2 spectra, and the behavior between 370 and 410 nm indicated no significant absorption by BrCl. During the subsequent 40 min, the concentrations of Br_2 and Cl_2 decreased strongly, and an equivalent increase in BrCl was observed. After several hours, the constant spectrum attained could be interpreted quantitatively in terms of

[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).

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

the three halogen molecules with $[BrCl]^2/[Br_2][Cl_2] = 12$ (compared to a reported[5] value of 8 at 300°K). These observations did not establish the kinetics of BrCl formation but suggest that $k_3 \simeq k_1/150$.

Reactions 1 and 2 are so rapid that homogeneous atomic chain mechanisms are ruled out. As a further test, it was observed that no dark reaction occurred when HBr was replaced by H_2, but illumination with visible light led to a rapid reaction. Substitution of air for nitrogen as carrier gas also had no noticeable effect on the rate.

The kinetic data and the independence of reaction rate on cell diameter indicate that reactions 1 and 2 are indeed elementary bimolecular processes. If usually accepted values are used for collision frequencies, the activation energies are about 10 to 15 kcal/mol; these low values demonstrate that the mechanism[1] of the $H_2 + I_2$ reaction does not apply in this system.

The much slower reaction 3 has not yet been studied in detail, and Christie, Roy, and Thrush[6] thought it to be heterogeneous in another system. Our present data merely set an upper limit for the rate of the homogeneous reaction, but even that upper limit is at least two orders of magnitude slower than the rate in supposedly "inert" solvents like carbon tetrachloride, carbon disulfide, and perfluoroalkanes.[7]

The apparatus used for these exploratory measurements will not permit really reliable measurements of rate constants and activation energies; apparatus for such quantitative studies is now being constructed. Calculations indicate that self-heating during reaction (Draper effect[8]) will not seriously interfere with such measurements.

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(5) W. H. Evans, T. R. Munson, and D. D. Wagman, *J. Res. Natl. Bur. Stand.*, **55**, 147 (1955).

(6) M. I. Christie, R. S. Roy, and B. A. Thrush, *Trans. Faraday Soc.*, **55**, 1139 (1959).

(7) B. L. McKinney, observations at the University of Oregon.

(8) P. Goldfinger, G. Huybrechts, A. M. Mathieu-Van der Auwera, and D. Van der Auwera, *J. Phys. Chem.*, **64**, 468 (1960).

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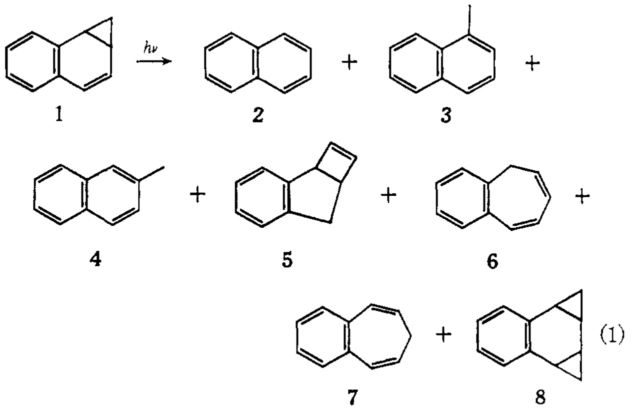
A Photochemical Berson–Willcott Bones Rearrangement[1]

Sir:

Recent interest in the photochemical reactivity of benzonorcaradienes[2] prompts us to report our work with the parent hydrocarbon.[3] Irradiation of a dilute, outgassed solution of benzonorcaradiene (**1**) in pentane with a 400-W GE mercury lamp through a Pyrex filter for 2 hr resulted in the formation of naphthalene (**2**, 46%), 1-methylnaphthalene (**3**, 7%), 2-methylnaphthalene (**4**, 4%), benzobicyclo[3.2.0]hepta-2,6-diene (**5**, 2%), 1,2-benzotropilidene (**6**, 2%), 3,4-benzotropilidene (**7**, *ca.* 2%), and bismethanonaphthalene (**8**, trace, eq 1). Recovered **1** represented 36% of the reaction mixture under these conditions.



Compounds **2**, **3**, **5**, and **6** were isolated pure by preparative glpc,[4a] while **7** was obtained admixed with **1** and **4**. After extended irradiation **4** could be isolated in pure form, since **1** and **7** ultimately rearranged. **2**, **3**, **4**, and **6**[3b] were identified by comparison of their nmr spectra and glpc retention times[4a] with those of authentic samples, while **8** was identified as reported previously.[3a] The presence of **7**, in the mixture with **1** and **4**, was deduced from its nmr spectrum by comparison with a known mixture of **1**, **4**, and **7**. In addition, its glpc retention time was identical with that of an authentic sample[3a] of **7**.[4b] **5** was characterized by comparison with an authentic sample prepared by the benzophenone-sensitized photolysis of indene and maleic anhydride,[5a] followed by $Pb(OAc)_4$ oxidative bisdecarboxylation.[5b,6]

The formation of **2** and **8** has been discussed previously.[3a] Swenton and Krubsack have recently provided analogy for the formation of **3** and **4**,[2a] and discussed the formation of this type of compound.

The formation of **6** can be rationalized by two different types of mechanisms. The first would be the reverse of the photochemical hydrogen migration by which **6** rearranges to **1**.[3b] The alternative possibility would employ a carbon skeletal rearrangement and no hydrogen shift. When 7,7-dideuteriobenzonorcaradiene (**9**)[7] was briefly irradiated[8] with uv light (5–10 min), it could be shown by nmr spectroscopy that the 1,2-benzotropilidene formed retained the CD_2 group. Thus, this result is inconsistent with a hydrogen

(1) (a) E. Vogel in "Aromaticity," Special Publication No. 21, The Chemical Society, London, 1967; (b) J. A. Berson and M. R. Willcott, III, *J. Amer. Chem. Soc.*, **88**, 2494 (1966).

(2) (a) J. S. Swenton and A. J. Krubsack, *ibid.*, **91**, 786 (1969); (b) E. Ciganek, *ibid.*, **89**, 1458 (1967).

(3) (a) M. Pomerantz and G. W. Gruber, *ibid.*, **89**, 6798 (1967); (b) M. Pomerantz and G. W. Gruber, *ibid.*, **89**, 6799 (1967).

(4) (a) A 10 ft × 0.25 in. column packed with 20% Carbowax 20 M on 60–80 mesh Chromosorb P, operated at 180°, was employed. (b) **7** could be partially separated from **1** and **4** with a 10 ft × 0.25 in. column packed with 20% TCEP on 60–80 mesh Chromosorb P operated at 175°.

(5) (a) W. Metzner, H. Partale, and C. H. Krauch, *Chem. Ber.*, **100**, 3160 (1967); (b) C. A. Grob, M. Ohta, E. Renk, and A. Weiss, *Helv. Chim. Acta*, **41**, 1191 (1958).

(6) An independent preparation has since appeared: (a) W. Metzner and K. K. Morgenstern, *Angew. Chem. Intern. Ed. Engl.*, **7**, 379 (1968); (b) W. Metzner and W. Hartmann, *Chem. Ber.*, **101**, 4099 (1968).

(7) M. Pomerantz and G. W. Gruber, *J. Org. Chem.*, **33**, 4501 (1968).

(8) Irradiations of 5–10-min duration produced *ca.* 5% of **2** and 90–95% of starting material (**1** or **9**). After 30 min there was *ca.* 27% of **2** and *ca.* 53% of **1** or **9**. Deuterium scrambling in the starting material in the former case was <5%. Thus the products, $5\text{-}d_2$ and $6\text{-}d_2$ would not, within experimental error, have shown scrambling.