Tetrahedron Letters No. 17, pp 1625 - 1628, 1972. Pergamon Press. Printed in Great Britain.

ACIDITY OF HYDROCARBONS. XLV. KINETIC ACIDITY OF ETHYLENE TOWARDS CESIUM CYCLOHEXYLAMIDE

M. J. Maskornick* and A. Streitwieser, Jr.,

Department of Chemistry, University of Califonria
Berkeley, California 94720

(Received in USA 10 March 1972; received in UK for publication 16 March 1972)

Despite the apparent simplicity and fundamental significance of ethylene as the parent alkene, estimates of its relative acidity cover a wide range. In his MSAD scale, Cram (1) considers ethylene to be more acidic than benzene whereas in his summary, Kosower (2) put ethylene 1 pK unit higher than benzene. Several experimental approaches have been used. Applequist and O'Brien (3) found equilibrium 1 in ether to have log K = -2.4; this result would seem to imply that vinyl anion is more stable than phenyl anion.

$$C_2H_3Li \ + \ C_6H_5I \ \rightleftharpoons \ C_2H_3I \ + \ C_6H_5Li \qquad \text{eq. 1}$$

On the other hand Dessy, et al., (4) from a related equilibrium between the mercury and magnesium derivatives in glyme found a reverse order of relative carbanion stabilities. In these reactions the position of equilibrium may depend not only on relative carbanion stability but also on differential solvation of the organometallic compounds; for example, vinyllithium is aggregated in THF and has consequent reduced reactivity (5). Finally, the polarographic reduction potentials of organomercury compounds have also suggested that ethylene is 1 pK unit more acidic than benzene (6). In this paper we report the relative kinetic acidity of ethylene in hydrogen isotope exchange with cesium cyclohexylamide (CsCHA) in cyclohexylamine (CHA) and conclude that the ion pair acidity of ethylene is *less* than that of benzene.

---

*National Science Foundation Fellow 1965-8; Petroleum Research Fund Fellow, 1968-9.

The volatility of ethylene forced modifications in our usual experimental technique. The reactor used is shown in Fig. 1. The fragile bulb was filled under argon with a known volume of stock cesium cyclohexylamide solution. The apparatus was assembled and a known volume of fresh CHA containing 0.06 M toluene-2-t was transferred in by bulb-to-bulb distillation. A known volume of ethylene-d_4 was quantitatively transferred in with liquid nitrogen. The reactor was equilibrated at 25° C, then shaken to break the bulb and initiate the exchange. At a specific time the lower stopcocks were opened to vent ethylene into the evacuated bulb. These stopcocks were then closed and 5 ml of water was introduced into the reactor to quench the standard compound. The toluene-2-t was then isolated and analyzed by liquid scintillation counting. The ethylene was analyzed for deuterium content at low voltage by attaching the sample bulb to the inlet of a CEC 130 mass spectrometer. Ten separate such one-point kinetic experiments were carried out each for a different time interval and covering the range between 5 and 60% exchange. For each experiment the actual exchange of ethylene was corrected for the distribution of ethylene between solution and vapor phases. A separate evaluation of the solubility of ethylene in CHA (7) gave 0.58 as the fraction of ethylene in the solution phase in the kinetic experiments.

By careful duplication of the amounts of CHA, CsCHA and the hydrocarbons in each run it was possible to get good pseudo first order rate constants ($k = 8.99 \pm 0.76 \times 10^{-4}$ sec^{-1} for C_2D_4 [rate of loss of -$\underline{d}_4$ species] and $2.73 \pm 0.24 \times 10^{-4}$ sec^{-1} for toluene-2-t). However, the advantage of having a standard, toluene-2-t, present is that the extent of reaction of one reactant can be compared directly with that of the other such that any variations in catalyst concentration do not enter in. Such a plot is shown in Fig. 2 which gives directly the rate ratio $k(C_2D_4)/k(C_7H_7T) = 3.39 \pm 0.24$.

This number is converted to a rate relative to benzene as follows: From the known rate of toluene-2-t relative to benzene-t, 0.20 (8), and the isotope effect for benzene, $k_D/k_T = 2.5$ (9), we derive $k(C_2D_4)/k(C_6H_5D) = 0.27$. This number must be divided by four to obtain the relative exchange rate of a single

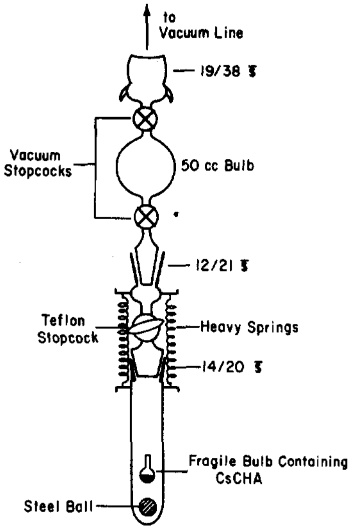

Fig. 1. Exchange reactor.

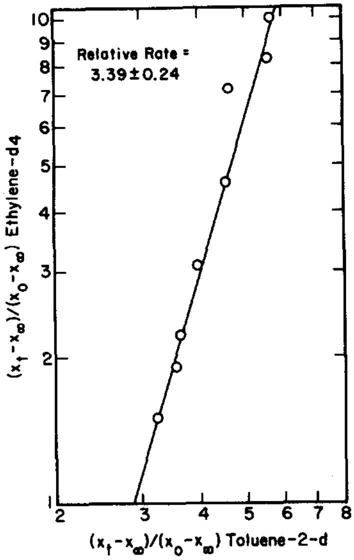

Fig. 2. Rate of loss of C_2D_4 compared to toluene-2-t with CsCHA.

deuterium in C_2D_4. To convert to a rate for C_2H_3D requires a knowledge of the secondary deuterium isotope effect. This effect is now known exactly but should not be far from 15% (10). Thus, $k(C_2H_3D)/k(C_6H_5D) = 0.078$ with an estimated uncertainty of about 10%.

It is of especial interest to apply to ethylene the following correlation that has worked so well with benzene (11) and triptycene (12) derivatives:

$$\log k/k_{\text{benzene}} = 0.608 \sum 1/r_{ij} - 1.565 \qquad \text{eq. 2}$$

where r_{ij} is the distance between the carbanion carbon and each other π-carbon in the system (13). In vinyl anion the field effect function, $\sum 1/r_{ij}$, has only a single term. Taking $r_{ij} = 1.34$ Å gives a predicted relative rate of 0.078, in excellent agreement with experiment. This agreement suggests that ethylene is part of the same Brønsted family as benzene in this exchange reaction and, therefore, that the relative equilibrium ion pair acidity is in the same direction as the relative kinetic acidity. To the extent that cesium carbanide ion pairs are adequate models for free carbanions, ethylene is at least 1 pK unit *less acidic* than benzene.

Acknowledgement. This research was supported in part by Grant no. GM-12855 of the National Institutes of Health, U.S. Public Health Service.

References

(1) D. J. Cram, "Fundamentals of Carbanion Chemistry," Academic Press, New York (1965); p. 19.

(2) E. M. Kosower, "An Introduction to Physical Organic Chemistry," J. Wiley and Sons, Inc., New York (1968); p. 27.

(3) D. E. Applequist and D. F. O'Brien, *J. Amer. Chem. Soc.,* 85, 743 (1963).

(4) R. E. Dessy, W. Kitching, T. Psarras, R. Salinger, A. Chen and T. Chivers, *J. Amer. Chem. Soc.,* 88, 460 (1966).

(5) R. Waack and P. E. Stevenson, *J. Amer. Chem. Soc.,* 87, 1183 (1965).

(6) K. P. Butin, I. P. Beletskaya, A. N, Kashin and O. A. Rentov, *J. Organomet. Chem.,* 10, 197 (1967).

(7) T. A. Keevil and D. R. Taylor, unpublished results.

(8) A. Streitwieser, Jr., R. A. Caldwell, R. G. Lawler and G. R. Ziegler, *J. Amer. Chem. Soc.,* 87, 5399 (1965).

(9) A. Streitwieser, Jr. and R. A. Caldwell, *J. Amer. Chem. Soc.,* 87, 5394 (1965).

(10) A. Streitwieser, Jr. and D. E. Van Sickle, *J. Amer. Chem. Soc.,* 84, 254 (1962).

(11) A. Streitwieser, Jr. and R. G. Lawler, *J. Amer. Chem. Soc.,* 87, 5388 (1965).

(12) A. Streitwieser, Jr. and G. R. Ziegler, *J. Amer. Chem. Soc.,* 91, 5081 (1969).

(13) Note that this equation results from our latest least squares analysis and differs slightly from those given previously.