Electron Exchange between Benzene Radical Anion and Neutral Benzene

Sir:

We have measured the second-order rate constant for reaction 1 using esr exchange narrowing techniques.[1,2]

$$[C_6H_6]^{-1} + [C_6H_6]^0 \overset{k}{\rightleftharpoons} [C_6H_6]^0 + [C_6H_6]^{-1} \quad (1)$$

Benzene anion was prepared in 2:1 tetrahydrofuran (THF) and 1,2-dimethoxyethane (DME) mixtures, containing excess benzene, by Na-K alloy reduction.[3]

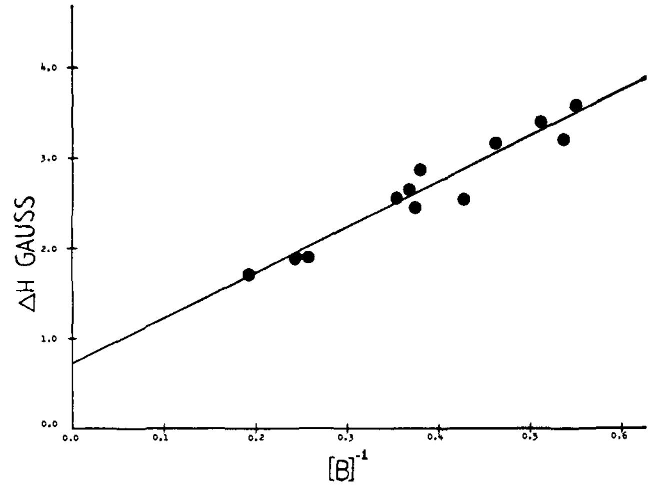

Figure 1. Least-squares plot of ΔH (in gauss) *vs.* reciprocal benzene concentration in moles per liter. Each point represents a separate preparation of $[C_6H_6]^{-1}$.

Neutral benzene concentrations were measured relative to the known DME volume by vpc analysis after completion of esr examination.[4] Samples generally remained stable between −10 and +20° for many hours. Above 20° decomposition usually caused loss of the esr signal in 30 to 60 min.[5]

Figure 1 illustrates the linear behavior required by the equation[1] $k = 2.03 \times 10^7 \nabla / \Delta H[B]$. ∇ is the spectral second moment calculated from a_H for benzene (in square gauss), ΔH is the exchange narrowed line breadth due to the electron-transfer process (in gauss), and [B] is the neutral benzene molarity. ΔH values were corrected for modulation effects. Line-breadth contributions due to spin-spin broadening and other broadening processes could not be measured directly since solutions simultaneously dilute in both $[C_6H_6]^{-1}$ and $[C_6H_6]$ were unstable in the temperature range −15 to 35°. However, results of Miller and Adams[6] suggest spin-spin broadening contributions should be small at the radical-anion concentrations we employed. Inability to correct our ΔH values for such broadening contributions probably explains the shift of our curve away from the origin ($[B]^{-1} = 0$) in Figure 1. However, only the slope of the curve is important for determining k.

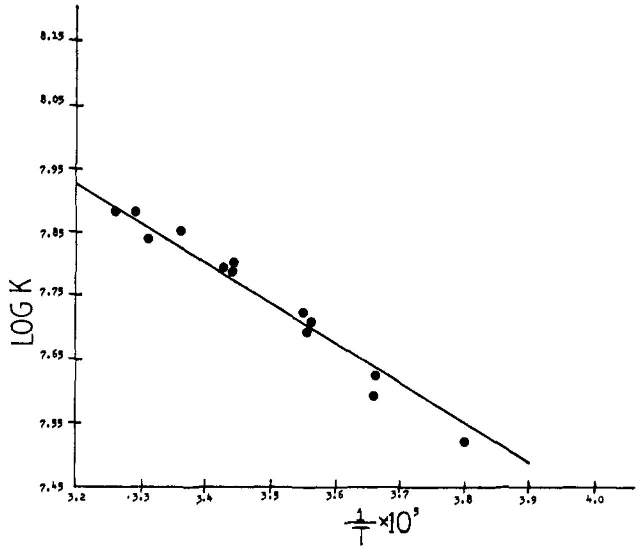

Figure 2. Arrhenius plot for reaction 1 for the range −15 to 35°. The straight line represents a least-squares plot of data from three different experiments.

$a_H = 3.60 \pm 0.06$ gauss was used to calculate $\nabla = 19.1$ (gauss)^2 at 18°.[7] This value of ∇ and the least-squares slope from Figure 1 yields $k = (7.7 \pm 0.8) \times 10^7\ M^{-1}\ \text{sec}^{-1}$ at 18°. Below −15° samples with $[B]^{-1} = 0.2$–0.6 were not in the exchange narrowed limit. $E^{\ddagger} = 2.8 \pm 0.6$ kcal/mole was found for the apparent activation energy of reaction 1 (Figure 2).

Our data suggest that we have measured k for process 1 because (a) $E^{\ddagger} < \sim 5$ kcal/mole strongly implies negligible contact ion pair electron exchange with neutral molecules,[1,8] and (b) only a single exchange narrowed line was observed in our experiments, whereas two superimposed lines are often observed if a second rate process of equal importance occurs simultaneously in the system.[1]

Relative to large radical anions participating in electron-transfer reactions, *e.g.*, the anthracene-anthracenide system [$k = (1.2 \pm 0.1) \times 10^9\ M^{-1}\ \text{sec}^{-1}$, $E^{\ddagger} =$

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[1] (a) R. Chang and C. S. Johnson, Jr., *J. Am. Chem. Soc.*, **88**, 2338 (1966); (b) *J. Chem. Phys.*, **46**, 2314 (1967).

[2] T. Miller, R. N. Adams, and P. M. Richards, *ibid.*, **44**, 4022 (1966).

[3] (a) M. T. Jones, *J. Am. Chem. Soc.*, **88**, 174 (1966). (b) Other workers have observed benzene anion under a variety of conditions; see T. R. Tuttle and S. I. Weissman, *ibid.*, **80**, 5342 (1958); J. R. Bolton and A. Carrington, *Mol. Phys.*, 4, 497 (1961); S. P. Solodovnikov, *J. Struct. Chem.* (USSR), 2, 282 (1961).

[4] A standard curve was constructed from vpc recorder traces of solutions having a 2:1 THF-DME volume ratio and containing various DME-benzene volume ratios. All benzene volumes in actual samples were obtained relative to the fixed DME volume (determined by measurement in a calibrated side arm of the apparatus and assumed constant in a given experiment) by measuring the DME-benzene peak height ratios and comparing with the standard curve. Standard samples gave results with ±5% of the true volume ratios.

[5] Decomposition often imparted a yellow-green cast to the initially blue or blue-green solutions. Occasionally a fine gray-white precipitate appeared. However, this did not seem to affect our rate data. Some samples were kept for 20–30 days at −10°. Repeated warming and cooling of the solutions, in contact with small floating bits of alloy, had no apparent effect on decomposition rates of $[C_6H_6]^{-1}$ in the system. At low temperature (below ∼−30°) the typical seven-line benzene spectrum was always obtained. ΔH determinations were made at intervals as long as 15 hr apart for some samples (kept at −10° during such intervals) and little change in ΔH could be found, indicating that most decomposition occurred in the initial reduction process.

[6] Spin count comparisons using DPPH solutions as standards indicated $[C_6H_6]^{-1} \sim 10^{-4}$–$5 \times 10^{-4}\ M$ in our experiments. Experiments by T. A. Miller and R. N. Adams, *J. Am. Chem. Soc.*, **88**, 5713 (1966), lead us to believe spin-spin corrections for $[C_6H_6]^{-1} \sim 10^{-4}\ M$ should be less than 0.2 gauss.

[7] The monotonic decrease of a_H noted in ref 3a continues above −50°. Broadening effects prevent following a_H accurately above −30°, and $a_H = 3.60 \pm 0.06$ gauss represents linear extrapolation to 18°. More accurate determination of ∇ could change our values for k but certainly by no more than 5–10%. ∇ derived from this value was used in all calculations between −15 and +35°.

[8] N. Hirota and S. I. Weissman, *J. Am. Chem. Soc.*, **86**, 2537 (1964); E. deBoer and C. MacLean, *J. Chem. Phys.*, 44, 1334 (1966).

3 kcal/mole[9]] or the tris-*p*-nitrophenylmethide–tris-*p*-nitrophenylmethyl system ($k \sim 10^9\ M^{-1}\ \text{sec}^{-1}$, $E \sim$ 0.9–2 kcal/mole, depending on metal ion and solvent[10]), we note that k for reaction 1 is considerably smaller, although $E^{\neq}$ remains ~3 kcal/mole. It has been suggested that most simple, unsubstituted radical anions exchange electrons at or near the bimolecular diffusion-controlled limit and significantly lower rates only occur if the anion and its neutral precursor differ substantially in structure.[1b,11] This does not seem to be the case for $[C_6H_6]^{-1}$–$[C_6H_6]$ exchange. We interpret the small k for benzene to be due to an effect significantly different from the larger anion systems and most probably associated with higher specificity in the anion–solvent interactions for the smaller ion. This might be expected due to higher surface charge density on benzenide ion as compared to anthracenide ion or tris-*p*-nitrophenylmethide ion.

The rate data reported here should be of immediate interest for comparison with other information on structurally more complicated anion radicals. Formulation of a detailed theory of electron transfer in aromatic radical systems requires knowledge of substituent effects on k, and the benzene rate constant provides an important reference point for measurements in this field.[12]

(9) N. Hirota, Ph.D. Thesis, Washington University, St. Louis, Mo., 1963, pp 107–108.

(10) M. T. Jones and S. I. Weissman, *J. Am. Chem. Soc.*, **84**, 4269 (1962).

(11) C. S. Johnson, Jr., "Advances in Magnetic Resonance," Vol. I, Academic Press Inc., New York, N. Y., 1965, p 33.

(12) All esr measurements were made with a JEOLCO 3BSX spectrometer equipped with linear field sweep (Hall element controlled) and operating with 100-kc field modulation.

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Vibrational *vs.* Translational Activation in the H_2,H_2 and H_2,D_2 Exchange Reactions[1]

Sir:

The $H_2 + D_2 \rightleftarrows 2HD$ reaction is of considerable interest because it is the simplest example of an elementary process in which two atoms (or fragments) are exchanged in the collision of a pair of molecules. Moreover, Bauer and his co-workers[2] have recently focused attention on this reaction by the suggestion that the energy needed to cross the activation barrier is provided only by the vibrational energy of the colliding molecules and that the translational energy of relative motion does not contribute.[3] We report here some results of a quasi-classical trajectory study for the H_2,H_2 exchange reaction with particular emphasis on the importance of translational and vibrational energy. The calculation, which is a generalization of previous work on the (H,H_2) exchange reaction,[4] employs an approximate potential surface obtained by a semiempirical valence-bond method of the London–Eyring–Sato type.[5,6] On this surface the saddle-point configuration for the exchange reaction is a square with side 1.970 au, the barrier height being equal to 62.7 kcal/mole.[7] By Monte Carlo averaging over collision trajectories, the total reaction cross section was determined as a function of the initial vibrational states (v, v') of the two molecules and their initial relative kinetic energy. A supplementary study was made of the rectangular (D_{2h}) collisions, which proceed through the lowest energy path of the potential surface.

For D_{2h} reactions, the relative translational energy thresholds $E_R{}^{\circ}$ are 50.7, 31.4, and 19.8 kcal/mole for both molecules in the zeroth, first, and second vibrational state, respectively. In the three-dimensional calculation the thresholds are slightly above the D_{2h} results (*e.g.*, $v = v' = 0$, $E_R{}^{\circ} = 52.5$ kcal/mole; $v = v' = 2$, $E_R{}^{\circ} = 21.8$ kcal/mole). For $v = v' = 0$ in the D_{2h} case, the $E_R{}^{\circ}$ value corresponds to an energy (translation plus zero-point vibration) of 63.1 kcal/mole. Thus, about 99% of the total energy is available for reaction and both translational and vibrational energy must contribute. For the three-dimensional case, the corresponding figure is 97% of the system energy if rotational energy is excluded.[8] In higher vibrational states there is an increase in the total energy at threshold (*e.g.*, for $v = v' = 2$, the energy is 78.5 kcal/mole in D_{2h} collisions and 80.5 kcal/mole in three-dimensional collisions). It appears that ~98% of the translational energy is available (independent of v and v'), while the percentage of the vibrational energy E_v available varies approximately as [94 − 246E_v (au)]. This behavior contrasts sharply with models assuming vibrational adiabaticity; *e.g.*, for the D_{2h} collisions, 71% of the vibrational energy would be predicted to be available.[4,9]

The rate constant k_{st} (v, v', T) for molecules with vibrational quantum numbers (v, v') was calculated as a function of temperature by integrating the reaction cross section S_r (E_R, v, v', T) over a Boltzmann distribution for the translational energy. The contribution k_B (v, v', T) of the (v, v') state to the total rate constant $K(T)$ was evaluated by weighting k_{st} with the vibrational Boltzmann distribution. Table I lists some k_{st} and k_B values for 1600°K. By interpolating or extrapolating k_B for the (v, v') states not explicitly calculated and then summing over v and v', the total rate constant $K(T)$ was

(1) Supported in part by a contract with the U. S. Atomic Energy Commission and by a grant from the Petroleum Research Fund of the American Chemical Society.

(2) S. H. Bauer and E. L. Resler, Jr., *Science*, **146**, 1045 (1964); S. H. Bauer and E. Ossa, *J. Chem. Phys.*, **45**, 434 (1966).

(3) S. H. Bauer, D. Marshall, and J. Baer, *J. Am. Chem. Soc.*, **87**, 5514 (1965).

(4) M. Karplus, R. N. Porter, and R. D. Sharma, *J. Chem. Phys.*, 40, 2033 (1964); **43**, 3259 (1965).

(5) F. London, *Z. Elektrochem.*, **35**, 552 (1929); H. Eyring and M. Polanyi, *Z. Physik. Chem.* (Leipzig), **B12**, 279 (1931); S. Sato, *J. Chem. Phys.*, **23**, 592, 2465 (1955); F. O. Ellison, N. T. Huff, and J. C. Patel, *J. Am. Chem. Soc.*, **85**, 3544 (1963); R. N. Porter and M. Karplus, *J. Chem. Phys.*, 40, 1105 (1964); J. K. Cashion and D. R. Herschbach, *ibid.*, 40, 2358 (1964).

(6) A very similar surface has been proposed by R. B. Abrams, J. C. Patel, and F. O. Ellison, Abstracts, 151st National Meeting of the American Chemical Society, Pittsburgh, Pa., March 1966, Abstract N-33.

(7) *Ab initio* configuration–interaction molecular orbital calculations with 1s and 1s′ orbitals on each hydrogen suggest that the saddle-point configuration may be a rhombus or a rhomboid. However, since the resulting barrier height is greater than the energy required for the process $2H_2 \rightarrow H_2 + 2H$, no meaningful conclusions can be drawn. Improved calculations with extended basis sets are in progress. We thank Dr. R. Hoffmann, Dr. J. A. Pople, and Dr. I. Shavitt for suggestions and discussions on this point and Dr. R. M. Stevens for collaboration on these calculations.

(8) For the three-dimensional case, rotational energy is present for many of the collisions, in accord with the Boltzmann weighting used in the Monte Carlo averages. However, this appears to have only a small effect on the threshold.

(9) R. A. Marcus, *J. Chem. Phys.*, 41, 610 (1964); **45**, 4500 (1966).