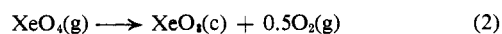


XeO₃. The standard heat of formation of XeO₃(c) has been determined⁶ to be 96 ± 2 kcal. mole⁻¹; hence the heat of the reaction



would be -58 kcal. mole⁻¹. The agreement of the observed Xe:O₂ ratio with the theoretical indicates either that reaction 2 did not occur to any significant extent or that the XeO₃ produced was itself subsequently decomposed to the elements. Any production of XeO₃ in the cell I and subsequent detonation by the XeO₄ explosion would introduce no error since the sum heat would still be that of reaction 1. Any XeO₃ deposited in the capillary and subsequently exploded would introduce an error since its heat would not be delivered to the calorimeter but the xenon and oxygen produced would be measured, and in the expected ratio. Three factors suggest that this possible error cannot have been serious: the short residence time of XeO₄ in the capillary while flowing to the cell; the consistency of the five runs; and the fact that runs 1, 2, and 3 used an ordinary glass high-vacuum stopcock lubricated with Kel-F grease while runs 4 and 5 used a Springall greaseless diaphragm-type valve with Viton A diaphragm; absorption in the grease or reaction with the diaphragm are thus unlikely to have been significant.

Using 119 kcal. mole⁻¹ for the dissociation energy of oxygen,⁶ the thermochemical bond energy in XeO₄ is 21.1 kcal. For XeO₃, the value is 27.5 - Δ*H*_{sub}/3; the vapor pressure of XeO₃ is very low and Δ*H*_{sub} is unknown. However, Studier⁷ observed the molecular mass spectrum of XeO₃ with a source at room temperature, with the intensity increasing rapidly as the temperature was raised slightly; an estimate of 30 ± 10 kcal. mole⁻¹ for Δ*H*_{sub}(XeO₃) might be made. The Xe-F thermochemical bond energies are approximately 28 kcal.⁸ for XeF₂, 30⁹ or 32¹⁰ for XeF₄, and 32¹⁰ for XeF₆. Thus the energy of the Xe=O bond is substantially less than that of Xe-F, but like Xe-F varies little with the oxidation number of the xenon.

From these bond energies, one may estimate -6 kcal. mole⁻¹ for the standard heat of formation of gaseous XeOF₄, and +56 kcal. mole⁻¹ for XeO₂F₂.

(5) S. R. Gunn, "Noble Gas Compounds," H. H. Hyman, Ed., University of Chicago Press, Chicago, Ill., 1963, p. 149.

(6) T. L. Cottrell, "The Strengths of Chemical Bonds," 2nd Ed., Butterworth Scientific Publications, London, 1958.

(7) M. H. Studier, unpublished observations, Argonne National Laboratory, 1964.

(8) B. Weinstock, E. E. Weaver, and C. P. Knop, ref. 5, p. 50.

(9) S. R. Gunn and S. M. Williamson, ref. 5, p. 133.

(10) L. Stein and P. Plurien, ref. 5, p. 144.

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Received March 29, 1965

Equilibria between Metallic Sodium and Aromatic Hydrocarbons¹

Sir:

In the course of investigations of the formation² and degradation kinetics of vinyl aromatic polyradical

(1) This paper represents one phase of research performed by the Jet Propulsion Laboratory, California Institute of Technology, sponsored by the National Aeronautics and Space Administration, Contract NAS7-100.

(2) A. Rembaum and J. Moacanin, *J. Polymer Sci.*, **B1**, 41 (1963).

anions³ a pronounced temperature effect was observed on the visible spectra of the poly(vinylbiphenyl)- and poly(N-vinylcarbazole)-sodium complexes, as well as on the complexes of the corresponding ethyl-substituted aromatic hydrocarbons dissolved in tetrahydrofuran (THF). The temperature effect could not be attributed to variation of volume changes due to thermal contraction or expansion, since the apparent extinction coefficient and also the free spin concentration as determined by the electron spin resonance technique³ (e.s.r.) varied by as much as a factor of six to seven. This loss of paramagnetism with increase of temperature was previously assumed⁴ to be a result of a disproportionation reaction leading to the formation of dinegative ions. Our data indicate that this interpretation does not apply to our systems. Although the intensity of the e.s.r. signal increased markedly with temperature decrease, the wave lengths of the absorption peaks in the visible part of the spectrum remained unchanged over a wide temperature range, suggesting that no new complexes were being formed. Since metallic sodium does not dissolve in THF,^{3,5} these facts are therefore consistent with the postulated equilibrium⁶ between sodium and aromatic hydrocarbons; the equilibrium was confirmed by the isolation of pure sodium after warming to room temperature a THF solution of [N-ethylcarbazole]⁻Na⁺ or [4-ethylbiphenyl]⁻Na⁺ prepared at -70°. The phenomenon is completely reversible, with the sodium particles dissolving and the blue color darkening upon cooling.

Although equilibria between alkali metals and aromatic hydrocarbons have been considered previously⁷ and a reversible color change was noted,⁸ the influence of temperature on the extinction coefficients of charge-transfer bands exhibited by alkyl-substituted hydrocarbon radical anions has, to our knowledge, never been investigated, and the temperature-induced reversible precipitation of an alkali metal associated with an aromatic radical anion has not been observed.

In this communication we summarize the preliminary results of a quantitative study of the equilibria between sodium and some substituted aromatic hydrocarbons by a spectrophotometric technique.

The absorption spectrum of [N-ethylcarbazole]⁻Na⁺ recorded at three different temperatures in the wave length range of 300 to 500 mμ is shown in Figure 1. The charge-transfer band at 390 mμ shows a remarkable change with temperature, while the bands at 350 mμ and below change only slightly.⁹ The latter originate from electronic transitions which are not affected by the extra electron, in agreement with the interpretation given previously.¹⁰ The variation of the absorbance

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(5) F. Cafasso and B. R. Sundheim, *J. Chem. Phys.*, **31**, 809 (1959); F. S. Dainton, D. M. Wiles, and A. N. Wright, *J. Chem. Soc.*, 4283 (1960).

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(7) G. J. Hooijink, E. deBoer, P. H. Van der Meij, and W. B. Weijland, *Rec. trav. chim.*, **74**, 277 (1955); *ibid.*, **75**, 487 (1956).

(8) S. I. Weissman, *J. Am. Chem. Soc.*, **80**, 6462 (1958).

(9) The spectrum between 300 and 350 mμ (Figure 1) is identical with the spectrum of unreacted N-ethylcarbazole in this wave length range.

(10) D. E. Paul, D. Lipkin, and S. I. Weissman, *J. Am. Chem. Soc.*, **78**, 116 (1956).

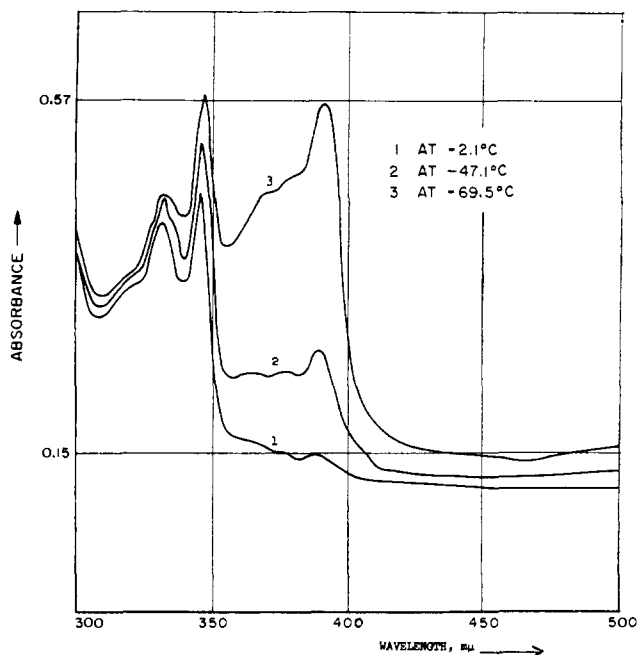


Figure 1. Absorption spectrum of [N-ethylcarbazole]⁻Na⁺ at three different temperatures.

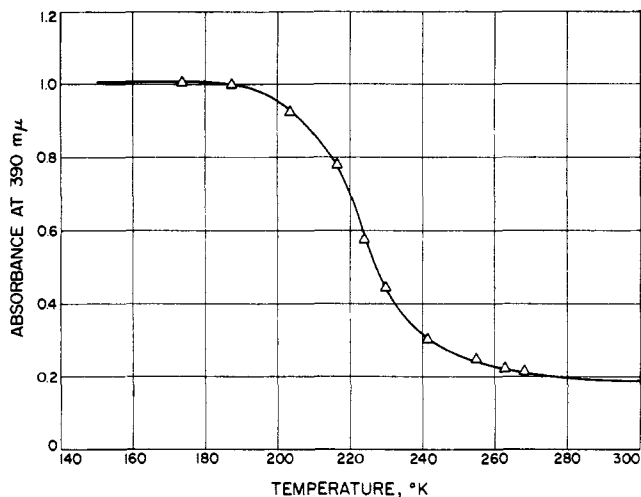


Figure 2. Absorbance of N-ethylcarbazole radical anion vs. temperature.

at 390 mμ with temperature is shown in Figure 2 and depicts more clearly the drastic change in absorbance which occurs within a temperature range of about 70°.

The value of the equilibrium constant at various temperatures can be determined from Figure 2, even without the knowledge of the molar extinction coefficient of the radical anion, assuming that Beer's law holds. Since a sodium titration has shown that every aromatic unit has acquired an electron at the lowest temperature, the low-temperature absorbance plateau (A_0) minus the base-line absorbance (A_B) is proportional to the total concentration of aromatic molecules, while A_t , the absorbance at any temperature, minus A_B , is proportional to the concentration of aromatic radical anions at that temperature. The equilibrium constant (K) thus becomes

$$K = \frac{A_t - A_B}{A_0 - A_t} \quad (1)$$

Plots of the values of this equilibrium constant as a function of temperature for three different species are shown in Figure 3. Excellent linearity is observed over wide concentration ranges, confirming the ion-pair concept.¹¹ The calculated enthalpy changes (ΔH° values) are -9200, -9000, and -7000 cal./mole for 4-ethylbiphenyl, N-ethylcarbazole, and poly(4-vinylbiphenyl) radical anions, respectively.¹²

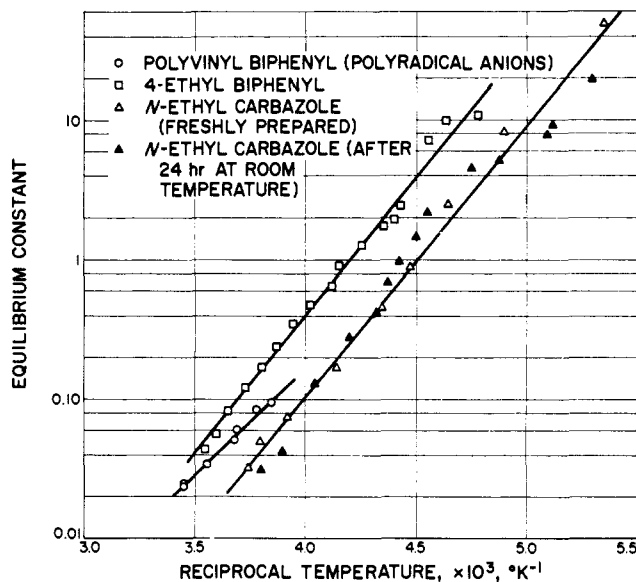


Figure 3. Log of equilibrium constant vs. reciprocal temperature.

An explanation can now be given for the well-known difficulty of forming the benzene radical anion at room temperature. The above results indicate that the benzene radical anion probably exhibits a similar behavior to N-ethylcarbazole as a function of temperature, but its characteristic curve which should resemble Figure 2 is probably displaced to a low-temperature region. By contrast, the relatively small variations of the extinction coefficient in the range of -60 to 30° of the spectrum of the naphthalene or biphenyl radical anion² probably indicate that their characteristic curves lie above room temperature.

The described results offer a relatively simple method for preparing very finely divided sodium particles in a number of solvents, a phenomenon which may have applications in organic syntheses and in polymer chemistry.

Acknowledgment. We wish to thank Dr. J. M. Flournoy for the e.s.r. spectra determination and Professor M. Szwarc for reading the manuscript and helpful suggestions.

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(12) The calculated entropy change for the N-ethylcarbazole-sodium equilibrium is unusually large (of the order of -40 e.u.), and this will be investigated further.

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Received March 5, 1965