

The data in Tables III and IV show that this is not the case, and therefore the episulfide-forming step must involve the participation of  $S(^1D)$  atoms.

It is also clear that  $S(^1D)$  atoms are less selective than  $(^3P)$  atoms. Upper limits for the relative rate constants are 1, 2.9, and 7.5 for ethylene, propylene, and isobutylene, respectively. The relative importance of  $S(^1D)$  addition cannot be evaluated from the present study. It is estimated that 70% or more of the episulfides are formed from singlet atoms. The data can best be rationalized by assuming that the same factors influence the rates of addition of both species; that is, the rate increases with increasing alkyl substitution in the olefin. A lowering in the activation energy and the consequent decrease in selectivity for the excited-atom reaction is not surprising, since the intersection of the corresponding potential energy surfaces in this case occurs at 26 kcal/mole higher energy and equivalently longer intermolecular separation. Assuming similar contours for the repulsive potentials, this results in

lowering the energy separation of the point of intersection from that of the separated olefin + S-atom surface, which determines the magnitude of the activation energy barrier.

In intermolecular competing reactions, the  $\pi$ -bond reactivity increases in the order ethylene < propylene < isobutylene, whereas the intramolecular competition between mercaptan and episulfide formation suggests that the  $\pi$ -bond reactivity in the series propylene, 2-butene, trimethylethylene, and tetramethylethylene (*vide supra*) is the same. The discrepancy can be resolved if it is assumed that in the  $\alpha,\beta$ -methylated ethylenes the methyl groups exert a steric hindrance, compensating for the increased reactivity of the  $\pi$  bond. Thus the interpretation of both  $S(^3P)$  and  $S(^1D)$  atom reactivity makes it necessary to invoke steric hindrances in methylated ethylenes.

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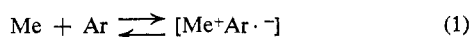
## Equilibria between Metallic Sodium and Aromatic Hydrocarbons<sup>1</sup>

A. Rembaum, A. Eisenberg, R. Haack, and R. F. Landel

*Contribution from the Jet Propulsion Laboratory, California Institute of Technology, Pasadena, California. Received October 29, 1966*

**Abstract:** The visible and electron spin resonance spectra of a series of alkyl-substituted aromatic hydrocarbons which were allowed to react with sodium in tetrahydrofuran solutions were investigated as a function of temperature. A marked increase in the optical density at the wavelengths of the charge-transfer peaks at low temperatures was found to be accompanied by an increase in free spin concentrations, both phenomena being reversible. The occurrence of sodium precipitation on raising the temperature and dissolution at low temperatures was also found to be reversible. These observations were interpreted as being the result of the shifts in the equilibrium of the reaction between sodium and the aromatic hydrocarbons. The electron affinity of the aromatic hydrocarbons as calculated by means of the Hückel MO theory was correlated with the experimentally determined  $\Delta H$  values.

Although the reaction between numerous aromatic hydrocarbons and alkali metals to yield intensely colored solutions in appropriate solvents has been known for a long time,<sup>2</sup> the effects of temperature on the optical absorption spectra of the resulting radical ions have not been investigated until recently.<sup>3-5</sup> Only in some materials has a very pronounced change in the absorption intensity as a function of temperature been observed, and this has been attributed to a shift in the equilibrium<sup>3,4a</sup> of the reaction



(1) (a) 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) H. D. Scott, J. F. Walker, and V. J. Hansley, *J. Am. Chem. Soc.*, **58**, 2442 (1936).

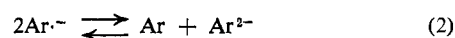
(3) A. A. Shatenshtein, E. S. Petrov, and M. J. Belousova, *Org. Reactivity*, **1**, 191 (1964) (in Russian).

(4) (a) A. Rembaum, A. Eisenberg, and R. Haack, *J. Am. Chem. Soc.*, **87**, 2291 (1965); (b) J. Hoijsink, N. H. Velthorst, and P. J. Zandstra, *Mol. Phys.*, **3**, 533 (1960).

(5) (a) T. E. Hogen-Esch and J. Smid, *J. Am. Chem. Soc.*, **88**, 307 (1966); (b) B. J. McClelland, *Chem. Rev.*, **64**, 301 (1964).

where Me is the alkali metal, Ar is the aromatic unit,  $Me^+$  is the metal cation,  $Ar \cdot^-$  is the aromatic free radical anion, and  $[Me^+Ar \cdot^-]$  represents either a tightly or loosely bound ion pair. It has also been shown<sup>4a</sup> that since the enthalpy for (1) is negative, precipitation of sodium dust occurs as the temperature is raised.<sup>6</sup>

Reactions of this type are usually carried out in aprotic organic solvents of relatively low dielectric constant and are known to be subject to various complications such as changes in solvation of the individual ions with temperature,<sup>3</sup> dissociation or formation of ion pairs or even higher aggregates,<sup>7</sup> and disproportionation according to



The disproportionation equilibrium 2, which was reviewed by McClelland,<sup>5b</sup> however, is generally of im-

(6) A practical application of this phenomenon is the preparation of sodium dispersions for synthetic purposes. Several grams of very reactive sodium were prepared by the use of N-ethylcarbazole.

(7) R. M. Fuoss and C. A. Krauss, *J. Am. Chem. Soc.*, **55**, 2387 (1933); N. Hirota and S. I. Weissman, *ibid.*, **86**, 2538 (1964); I. M. Brown, S. I. Weissman, and L. C. Snyder, *J. Chem. Phys.*, **42**, 1105 (1965).

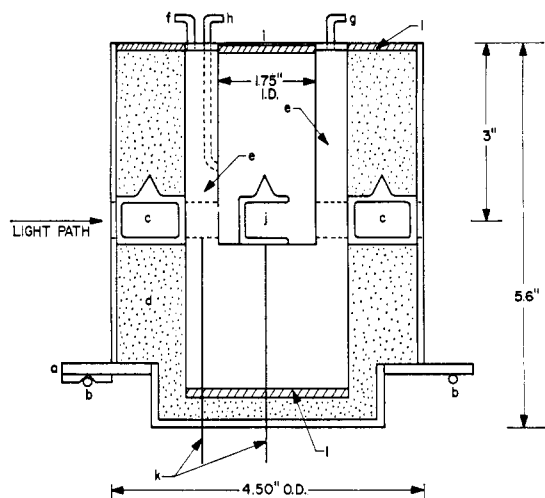


Figure 1. Cross section of temperature-controlled optical cell holder: (a) support plate, (b) sample compartment guide rods, (c) evacuated cylindrical silica cells, (d) Styrofoam insulation, (e) honeycombed aluminum insert with holes for circulation of coolant (for sample cell support and thermostating), (f) coolant inlet, (g) coolant outlet, (h) inlet for dry nitrogen to prevent frosting of sample cell, (i) cover of sample compartment, (j) sample cell, (k) thermocouple leads, (l) transite cover and base.

portance only in certain hydrocarbons of high electron affinity.<sup>4b</sup>

Shatenshtein<sup>3</sup> examined the equilibrium constant of eq 1 for naphthalene and biphenyl as a function of the solvent and the alkali counterion and showed that this equilibrium is very sensitive to the degrees of solvation, the solvation of the metal ions having a much greater effect on the equilibrium than the solvation of the aromatic radical ion.

In this paper we report an investigation of this equilibrium as a function of the nature of the aromatic moiety alone. Keeping the solvent and the counterion constant (using tetrahydrofuran (THF) as the solvent and Na as the alkali metal), most of the complications described above are reduced to a minimum for a series of substituted hydrocarbons of relatively low electron affinity.

In addition to a study of the equilibrium constants by use of spectrophotometry and electron spin resonance (esr) techniques, it is shown that metallic sodium gradually precipitates from the homogeneous solution as the temperature is raised, and that this process is reversible. Finally, since the electron affinity had previously been correlated with molecular orbital calculations of the lowest antibonding orbital of the aromatic species,<sup>8</sup> similar calculations are performed in this study. It is shown that the low values of  $\Delta H$  for reaction 1 can be correlated with the low electron affinities of aromatic hydrocarbons.

## Experimental Section

**Purification.** All aromatic hydrocarbons were purified by crystallization from appropriate solvents, by zone refining, or by preparative gas-liquid partition chromatography (glpc), and their purity was ascertained by means of a Wilkens glpc apparatus (Aerograph Hy-Fi Model 600).

N-Ethylcarbazole (Aldrich Chemical Co.) was recrystallized from absolute EtOH three times in the presence of activated charcoal. A zone-refined specimen of mp 69.5° was used with identical results.

(8) A. Maccoll, *Nature*, **163**, 178 (1949).

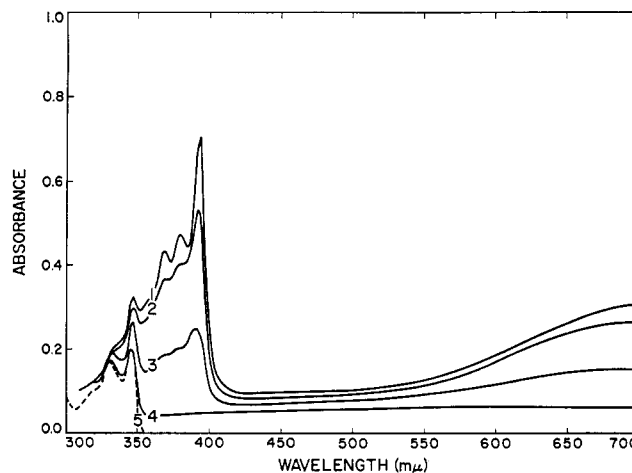


Figure 2. Optical absorption spectrum of the radical ion of N-ethylcarbazole at various temperatures (optical path  $5.0 \times 10^{-3}$  cm), in the presence of excess Na in THF: (1)  $-88^\circ$ , (2)  $-60^\circ$ , (3)  $-49^\circ$ , (4)  $12^\circ$ , (5) spectrum of N-ethylcarbazole ( $5.12 \times 10^{-5}$  M in ethanol, optical path 1.0 cm).

Biphenyl (Eastman Organic Chemicals) was recrystallized from absolute alcohol twice and vacuum sublimed (mp 69.0–70.0°).

4-Ethylbiphenyl (Research Organic Chemical Co.) was recrystallized from methanol but did not yield a material of sufficient purity. It was therefore passed six times through a multiple-zone refiner (14 ring heaters) and further purified by preparative gas-liquid partition chromatography (Aerograph Autoprep Model A-700, 5 ft  $\times$   $\frac{3}{8}$  in. SE30 column at 220°). Upon reaction with a pure sodium film in THF, this material (mp 32–34°) yielded a blue color at low temperature with no intermediate red color formation (absence of absorbance in the 480-mμ region of the spectrum). Specimens containing impurities showed an absorption band at 480 mμ, increasing in intensity with time.

4-Methylbiphenyl (Research Organic Chemical Co.), after three recrystallizations from absolute MeOH, yielded a material with mp 47.5–48.0°. 3-Methylbiphenyl (Fluka, A. G.) was vacuum distilled (bp 53.4° at 5 mm). 4,4'-Dimethylbiphenyl (Aldrich Chemical Co.) was recrystallized from ether (mp 119.0–119.8°).

Tetrahydrofuran (THF) was refluxed with sodium for a 24-hr period, distilled, and then stirred with Na-K alloy in the absence of air and redistilled before use. The preparation of dilute or concentrated solutions of radical ions in THF was accomplished by means of the well-established vacuum technique.<sup>9</sup>

**Apparatus.** A Model 14 Cary spectrophotometer was used for the determination of absorption spectra in the temperature range from  $-100$  to  $+50^\circ$ . A sample cell holder to fit the Cary sample compartment was constructed, as shown in Figure 1. The desired temperature was maintained at  $\pm 0.5^\circ$  by regulating the flow of dry nitrogen through a copper coil immersed in liquid nitrogen. Electron spin resonance spectra were recorded on the Varian V-4501 spectrometer at 9500 Mc/sec with high-frequency modulation (100 kc/sec). Samples were kept at constant temperature with the aid of a V-4547 variable-temperature accessory.

## Results

### Absorption Spectra as a Function of Temperature.

The optical density increase as a function of temperature is shown for N-ethylcarbazole (Figure 2) and 4-ethylbiphenyl (Figure 3). The characteristics of the spectra as the temperature was lowered for 4-methyl- and 3-methylbiphenyl were identical with those in Figure 3. The maximum absorption peak at room temperature was at 402 mμ for 4-ethyl-, 4-methyl-, and 3-methylbiphenyl. This was shifted, for all three hydrocarbons, to 411 mμ at  $-90^\circ$ . The absorption peaks at 330 and 348 mμ, showing little change with tempera-

(9) D. E. Paul, D. Lipkin, and S. I. Weissman, *J. Am. Chem. Soc.*, **78**, 116 (1956); P. Balk, G. I. Holjink, and J. W. H. Schreurs, *Rec. Trav. Chim.*, **76**, 813 (1957).

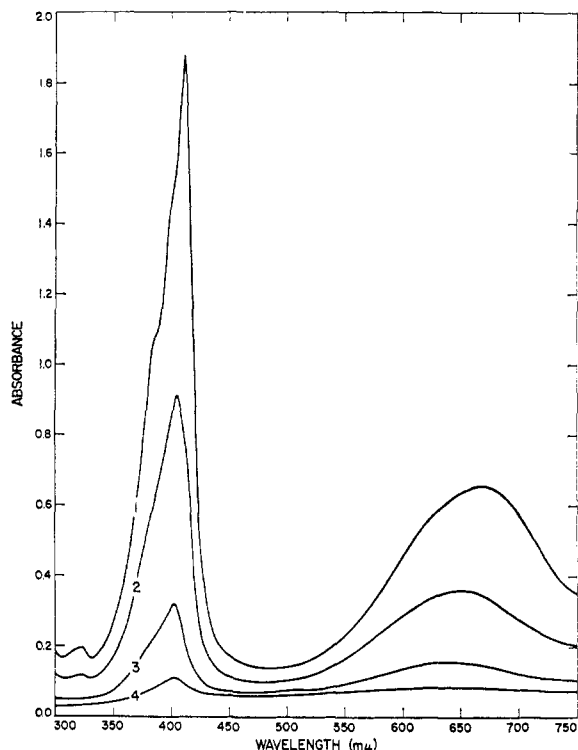


Figure 3. Optical absorption spectrum of 4-ethylbiphenyl radical ions at various temperatures in the presence of excess Na in THF (concentration of 4-ethylbiphenyl,  $7 \times 10^{-3} M$ ): (1)  $-95^\circ$ , (2)  $-34^\circ$ , (3)  $-12^\circ$ , (4)  $19^\circ$ .

ture, are due to N-ethylcarbazole itself, the absorption spectrum of which is also shown in Figure 2. The spectrum of the radical ion therefore retains the near-ultraviolet band of uncomplexed N-ethylcarbazole, which is not subject to large intensity changes, in contrast to the 389-mμ peak (Figure 2) attributed to the radical ion. The latter, however, undergoes a bathochromic shift of 4 mμ at low temperature. This type of shift was previously observed in the spectra of radical ions and carbanions and is very likely to be due to the extent of solvation of the cation at lower temperature.<sup>10</sup> This assumption is supported by the experimental findings of Garst and his collaborators<sup>11</sup> who studied the electronic transition energies of sodium benzophenone ketyls as well as by the work of Weissman<sup>12</sup> and others.<sup>5a</sup>

The temperature effect was investigated by reacting the alkyl-substituted aromatic hydrocarbons at  $-70$  to  $-90^\circ$  with a sodium mirror until no increase in the optical density of the maximum absorption peak was observed (about 25 min). Parts of the optical cell (0.005 cm) outside the light path contained a film of sodium on the walls. This assured an excess of sodium at all times without interfering with optical measurements. The cells were kept at low temperature before the spectra were recorded.

The most pronounced changes of absorption as a function of temperature were observed with N-ethylcarbazole and 4-methylbiphenyl at 389 and 402 mμ, respectively, and are shown in Figure 4. Since the

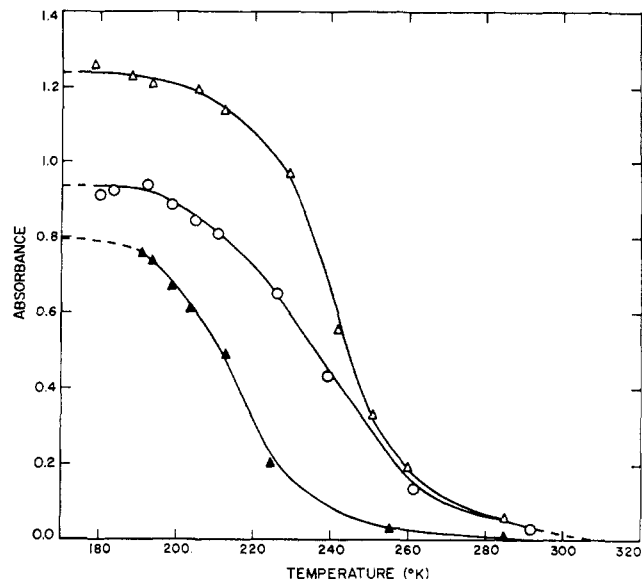


Figure 4. Absorbance of radical ions in the presence of excess Na as a function of absolute temperature.  $\lambda$  402 mμ, optical path  $5.0 \times 10^{-3}$  cm:  $\circ$ , 4-ethylbiphenyl ( $4.1 \times 10^{-3} M$ );  $\Delta$ , 4-methylbiphenyl ( $5.9 \times 10^{-3} M$ ).  $\lambda$  389 mμ, optical path  $5.0 \times 10^{-3}$  cm:  $\blacktriangle$ , N-ethylcarbazole ( $7.0 \times 10^{-3} M$ ).

curves of Figure 4 could be reproduced after leaving the solutions in the optical cells at a temperature of  $25^\circ$  for 24 hr, it may be concluded that no chemical reactions have taken place during the time of measurement. This was confirmed by analyzing the solutions by means of glpc. The glpc analysis showed the presence of the original component and the absence of any new species. The stability of THF solutions of radical ions ( $10^{-5} M$ ) of N-ethylcarbazole and alkyl-substituted biphenyls depended on the purity of the hydrocarbons. Well-purified specimens showed good stability, the decrease of radical ion concentration at  $25^\circ$  being of the order of only 5% after 90 hr as measured by the decrease of the optical density. At higher temperatures a faster decay was observed; e.g., N-ethylcarbazole radical ion concentration decreased to approximately one-half of its original value after 60 hr at  $50^\circ$ .

**Stoichiometry.** Determinations of the sodium concentration of THF solutions by titration with 0.1 N HCl showed practically 100% reaction (with the exception of 4,4-dimethylbiphenyl) at  $-75$  to  $-80^\circ$  for N-ethylcarbazole and substituted biphenyls. The results of sodium analyses are shown in Table I, the

Table I. Determination of Sodium Concentrations<sup>a</sup>

Hydrocarbon	Temp, $^\circ C$	$C_H$ , M	$C_{Na}/C_H$
4-Methylbiphenyl	5.5	0.106	0.26
	$-17.0$	0.106	0.65
	$-40$	0.106	0.84
	$-76$	0.006	0.95
N-Ethylcarbazole	$-48$	0.082	0.23
	$-63$	0.082	0.55
	$-65$	0.007	0.80
	$-70$	0.1	0.97
4-Ethylbiphenyl	$-60$	0.014	0.95
	$-76$	0.007	1.09

<sup>a</sup>  $C_H$  = molar concentration of hydrocarbon;  $C_{Na}$  = molar concentration of sodium.

(10) H. W. Carter, B. J. McClelland, and E. Warhurst, *Trans. Faraday Soc.*, **56**, 455 (1960); M. T. Jones and S. I. Weissman, *J. Am. Chem. Soc.*, **84**, 4269 (1962).

(11) J. F. Garst, D. Walmsley, C. Hewitt, W. R. Richards, and E. R. Zabolotny, *ibid.*, **86**, 412 (1964).

(12) N. M. Atherton and S. I. Weissman, *ibid.*, **83**, 1330 (1961).

**Table II.** Enthalpies and Other Parameters for the Equilibrium between Sodium and Some Aromatic Hydrocarbons

Hydrocarbon	$-\Delta H$		Resonance integral coefficient of the 1vmo, $X_{n+1}$	Calculated reduction potential, $-\epsilon_{1/2}$ , ev/molecule
	kcal/mole	ev/molecule		
4,4-Dimethylbiphenyl	$5.8 \pm 1.0$	$0.25 \pm 0.04$	-0.861	3.04
4-Methylbiphenyl	$8.1 \pm 0.8$	$0.35 \pm 0.03$	-0.776	2.82
3-Methylbiphenyl	$9.0 \pm 0.9$	$0.39 \pm 0.04$	-0.711	2.66
N-Ethylcarbazole	$8.8 \pm 0.9$	$0.38 \pm 0.04$	...	...
4-Ethylbiphenyl	$9.2 \pm 0.9$	$0.40 \pm 0.04$	...	...
Biphenyl	$11.2 \pm 0.5^a$	$0.49 \pm 0.02$	-0.705	2.64
Naphthalene	$12.0 \pm 0.5^a$	$0.52 \pm 0.02$	-0.618	2.42

<sup>a</sup> From ref 3.

$C_{Na}/C_H$  ratios below  $-70^\circ$  indicating essentially complete conversion to radical ions.

The molar extinction coefficients (average of five determinations) for N-ethylcarbazole at  $389\text{ m}\mu$ , 4-methylbiphenyl at  $402\text{ m}\mu$ , and 4-ethylbiphenyl at  $402\text{ m}\mu$  were found to be equal to 15,600, 41,800, and 42,100, respectively.

**Electron Spin Resonance (Esr).** The esr spectrum of N-ethylcarbazole (Figure 5) in the presence of unreacted sodium film increased in intensity with decrease of temperature. All attempts to resolve completely the spectrum of Figure 5 failed. The intensity of an over-modulated spectrum, consisting of a single line, was seven times greater at  $-70^\circ$  than at  $25^\circ$ , and this change was also reversible.

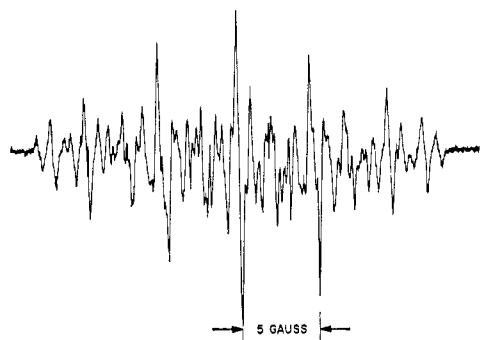


Figure 5. First derivative of the esr absorption spectrum of a dilute solution ( $10^{-4} M$ ) of the radical anion of N-ethylcarbazole reduced by sodium in THF at  $-50^\circ$ .

Although the lack of complete resolution of the hyperfine structure makes the theoretical interpretation difficult, a general analysis of the spectrum shows that no sodium splittings are present, and the same applies to the esr spectra of 4-methyl- or 4,4-dimethylbiphenyl. It should be noted that according to recent extensive esr investigations, the absence of alkali metal splittings does not exclude the possibility of ion pairing.<sup>13,14</sup>

### Interpretation of Results

The spectrophotometric and analytical data as well as the reversible precipitation of  $Na^{4a}$  leave little doubt that the main phenomenon observed is an equilibrium between metallic sodium and the aromatic hydro-

(13) A. H. Reddoch, *J. Chem. Phys.*, **43**, 225 (1965).

(14) M. C. R. Symons, paper presented at the Symposium on Electron Spin Resonance Spectroscopy, Michigan State University, East Lansing, Mich., Aug 1-3, 1966.

carbons which yields radical ion pairs, although the possibility of other equilibria exists, as indicated by the small spectra shifts at low temperatures.

On the assumption that the accompanying equilibria (e.g., disproportionation or free ion formation) do not contribute to equilibrium 1 to a considerable extent, one can determine the equilibrium constant at various temperatures from spectrophotometric data such as shown in Figure 4. Since sodium analysis showed that every aromatic unit acquired an electron

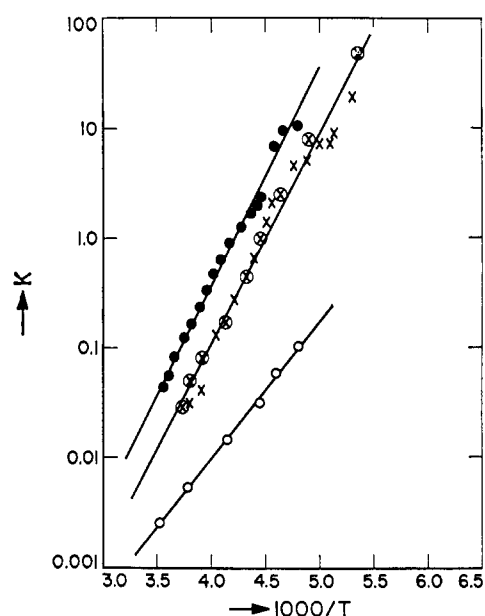


Figure 6.  $\log K$  vs.  $1/T$ :  $\bullet$ , 4-ethylbiphenyl;  $\circ$ , 4,4-dimethylbiphenyl;  $\times$ , N-ethylcarbazole;  $\otimes$ , N-ethylcarbazole (repeated after 24 hr).

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 ions at that temperature. The equilibrium constant ( $K$ ) thus becomes

$$K = \frac{A_t - A_B}{A_0 - A_B} \quad (3)$$

where the activity of the sodium is unity (since the sodium is solid).

Plots of the log values of this equilibrium constant vs.  $1/T$  for three different species are shown in Figure 6.

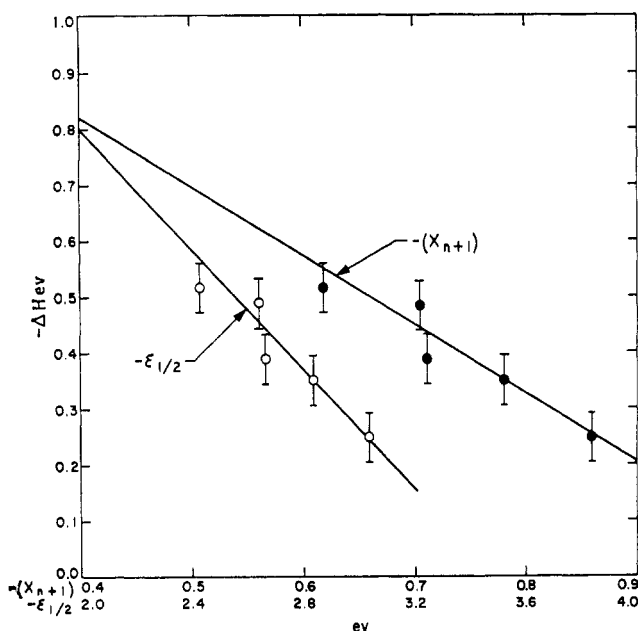


Figure 7. Change of enthalpy ( $-\Delta H$ ) for the formation of some radical ions listed in Table II vs. the coefficient of the resonance integral of the lvmO ( $-X_{n+1}$ ) and vs. the reduction potential ( $-\epsilon_{1/2}$ ).

Their linearity seems to justify the assumption that other equilibria occur only to a minor extent, if at all.<sup>15</sup>

From these plots the corresponding enthalpy values ( $\Delta H$ ) were obtained and are listed in Table II. Table II also contains the  $\Delta H$  values reported by Shatenshtein<sup>3</sup> for naphthalene and biphenyl.

According to a thermodynamic analysis outlined by Szwarc,<sup>16</sup> based on the energy balance for equilibrium 1,  $-\Delta H$  should depend on the following factors: (1) heat of sublimation and the ionization potential of the alkali metal, (2) the heats of solvation of cation and anion, (3) the energy of Coulombic interaction between the ions, and (4) the electron affinity of the aromatic hydrocarbon. Since in our experiments factors 1, 2, and 3 are not expected to vary to any considerable extent, the  $-\Delta H$  values should decrease as the electron affinity decreases.

The electron affinity is approximately equal to the negative of the energy of the lowest vacant molecular orbital<sup>17</sup>  $E_{n+1}$ . In the Hückel MO approximation the latter is expressed by

$$E_{n+1} = \alpha + X_{n+1}\beta \quad (4)$$

where  $\alpha$  is the Coulomb integral,  $\beta$  is the resonance in-

(15) Attempts to fit the experimental data in terms of equilibrium 1 plus the equilibrium involving dissociation of ion pairs into free ions were not successful.

(16) M. Szwarc, *Makromol. Chem.*, **35**, 132 (1960).

(17) G. J. Hoijtink, *Rec. Trav. Chim.*, **71**, 1089 (1952).

tegral between two adjacent carbon atoms, and  $X_{n+1}$  is the coefficient of the resonance integral ( $\beta$ ) of the lowest vacant molecular orbital (lvmO).

It is also true that the half-wave reduction potential ( $-\epsilon_{1/2}$ ) associated with an electron transfer from the alkali metal to the aromatic hydrocarbon is related to the electron affinity by

$$\epsilon_{1/2} = -X_{n+1}b + C' \quad (5)$$

(where  $b$  and  $C'$ ) are constants) if the solvation energy of the ions is assumed constant.<sup>17</sup> Excellent linear correlations between experimentally determined half-wave reduction potentials and those derived from eq 5 are reported in the literature.<sup>18-21</sup>

Since  $\alpha$ ,  $\beta$ ,  $b$ , and  $C'$  are constants here,  $\Delta H$  should therefore vary linearly with either  $X_{n+1}$  or the experimentally accessible quantity  $-\epsilon_{1/2}$ . To test this conclusion, the coefficients of the lowest vacant molecular orbitals for 4,4'-dimethylbiphenyl, 4-methylbiphenyl, and 3-methylbiphenyl were calculated on the basis of the Hückel theory using the inductive parameter of  $-0.5$  for the Coulomb integral of the substituted carbon atom as suggested by Wheland.<sup>22</sup> The half-wave reduction potential was then calculated using Hoijtink's values of  $-2.54$  and  $-0.85$  eV for  $b$  and  $C'$ , respectively.<sup>18</sup> These values were reported to give the best agreement for about 35 aromatic hydrocarbons (measured relative to the saturated calomel electrode).

The results, along with the known values for biphenyl and naphthalene, are given in Table II. The calculated MO coefficients and  $-\epsilon_{1/2}$  values agree with the expected low electron affinity of substituted biphenyls and consequently the relatively low enthalpy as compared with naphthalene and biphenyl. The comparison between  $\Delta H$  and  $X_{n+1}$  or  $\epsilon_{1/2}$  is shown in Figure 7. The relationships are indeed linear within experimental error and can be expressed as

$$-\Delta H = 1.2 + 1.1X_{n+1} \quad (6)$$

$$-\Delta H = 1.6 + 0.46\epsilon_{1/2} \quad (7)$$

According to eq 4 the absolute magnitudes of the slope of the  $X_{n+1}$  plot should be  $\beta$ , and similarly from eq 4 and 5 that of the  $-\epsilon_{1/2}$  plot should be  $\beta/b$ .

The observed ratio of the two slopes is 2.4, which is within experimental error of the expected value of 2.54.

Thus it is now possible to calculate at least approximately the heat of reaction for the electron-transfer step by means of the lcao coefficients of the molecular orbital  $X_{n+1}$ .

(18) G. J. Hoijtink, *ibid.*, **74**, 1525 (1955).

(19) G. I. Hoijtink and I. Schooten, *ibid.*, **72**, 692 (1953).

(20) G. I. Hoijtink, I. Schooten, E. de Boer, and W. I. Aalbersberg, *ibid.*, **73**, 355 (1954).

(21) I. Bergman, *Trans. Faraday Soc.*, **50**, 829 (1954).

(22) G. W. Wheland and L. Pauling, *J. Am. Chem. Soc.*, **57**, 2086 (1935).