

available for both. The similarity of the  $H_0$  dependence on water activity for the two acids is truly remarkable, both sets of data following one curve to well within the experimental uncertainty in  $H_0$  over most of the range. Thus the observed more rapid increase in the acidity of perchloric acid is reflected pre-

cisely in a correspondingly more rapid decrease in the water activity of this acid, as compared to sulfuric acid.

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[CONTRIBUTION FROM THE RADIATION LABORATORY<sup>1</sup> AND THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF NOTRE DAME, NOTRE DAME, INDIANA]

## Mononegative Molecular Ions of Aromatic Hydrocarbons in $\gamma$ -Irradiated Organic Glasses

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The electronic spectra of the mononegative molecular anions of biphenyl, anthracene, phenanthrene, 1,2-benzanthracene, triphenylene, *o*-terphenyl, pyrene, triphenylethylene, tetraphenylethylene, cycloheptatriene, and hexamethylbenzene produced in  $\gamma$ -irradiated organic glasses at 77°K. have been investigated. Relative anion formation efficiencies have been determined. The spectrum of  $\gamma$ -irradiated perylene has been investigated and attributed to the perylene monopositive ion.

### Introduction

The mononegative molecular ions of some aromatic hydrocarbons (naphthalene, phenanthrene, etc.) have been prepared chemically<sup>2-5</sup> by the interaction of alkali metals with aromatic hydrocarbons in suitable solvents, and their qualitative interpretation has been made with the aid of the LCAO-MO method including configuration interaction.<sup>6</sup>

A general method has been developed recently for the spectrophotometric observation of intermediates produced and trapped in  $\gamma$ -irradiated media at 77°K. which has provided information about electron solvation, simple and dissociative electron attachment, and photo-detachment.<sup>7</sup> It is the purpose of this work to examine anion formation by  $\gamma$ -irradiation by extending this method to a series of aromatic compounds in which chemical methods have been previously employed and to determine the relative electron attachment efficiencies of these aromatic hydrocarbons.

### Experimental

**Solvents.**—Of primary consideration in the selection of 2-methyltetrahydrofuran (MTHF) as a solvent was the fact that it forms clear glasses transparent from the near-ultraviolet to the far-infrared, dissolves the aromatic hydrocarbons under investigation relatively well, and is chemically similar to the solvents used in chemical preparation. It was purified by passing through a column containing basic alumina (Woelm). Phillips pure grade 3-methylpentane (3MP) and 2-methylpentene-1 (2MP-1), which were used as solvents to a small extent, were also purified by passing through a column of silica gel.

**Solutes.**—The following materials were used as received: biphenyl, Monsanto (recrystallized from ethanol); anthracene, phenanthrene, *o*-terphenyl, triphenylethylene, and pyrene, East-

man White Label products; 1,2-benzanthracene, triphenylene, perylene, triphenylethylene, and tetraphenylethylene, Aldrich Chemical products.

The methods of  $\gamma$ -irradiation, dosimetry, and absorption spectrophotometry relevant to this work have been described elsewhere.<sup>7</sup> Unless otherwise indicated, the doses were approximately  $0.75 \times 10^{18}$  e.v./ml.

### Results and Discussion

$\gamma$ -Irradiation of organic glasses ejects electrons from the solvent and these appear to become attached through diffusion to solute or solvent molecules or else to recombine with positive ions. In pure MTHF at 77°K. a broad absorption appears extending from approximately 9000 to 16,000 Å. and with maxima at  $\sim 12,100$  and  $13,700$  Å. This absorption can be bleached by infrared light and is attributed to solvated electrons. In the presence of a small amount of biphenyl the anion absorption of biphenyl appears with a concomitant decrease of the solvated electron absorption. With concentrations of biphenyl as large as 0.15 mole % and at doses approximating  $0.75 \times 10^{18}$  e.v./ml. the solvated electron absorption disappears, while the biphenyl anion band acquires its limiting intensity (O.D. = 0.76 at 4100 Å.). The process is competitive in the sense that the ejected electrons divide themselves between solute and solvent molecules according to the efficiency of the solute for electron attachment and its concentration, and depending upon the positive hole mobility of the solvent.<sup>7</sup> In the presence of two different solutes X and Y the number  $N$  of anions  $X^-$  and  $Y^-$  formed is given by

$$N_X/N_Y = \sigma_X C_X / \sigma_Y C_Y \quad (1)$$

where  $\sigma_X$ ,  $\sigma_Y$  are electron-attachment cross sections of solute X and Y, respectively, and  $C_X$ ,  $C_Y$  are the corresponding concentrations. Since the optical density of absorption of a certain anion species is proportional to the number of anion species ( $N$ ), eq. 1 is easily transformed<sup>7b,d</sup> into

$$1/D_{Y^-} = 1/D_{Y^-}^0 + \sigma_X C_X / \sigma_Y D_e^0 C_Y \quad (2)$$

where  $D_{Y^-}$  is the O.D. of the anion of the reference solute (biphenyl, for example), and  $D_{Y^-}^0$  is the limiting O.D. of this anion.

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(7) (a) M. R. Ronayne, J. P. Guarino, and W. H. Hamill, *J. Am. Chem. Soc.*, **84**, 4230 (1962); (b) J. P. Guarino, M. R. Ronayne, and W. H. Hamill, *Radiation Res.*, **17**, 379 (1962); (c) M. Kondo, M. R. Ronayne, J. P. Guarino, and W. H. Hamill, *J. Am. Chem. Soc.*, **86**, 1297 (1964); (d) E. P. Bertin and W. H. Hamill, *ibid.*, **86**, 1301 (1964).

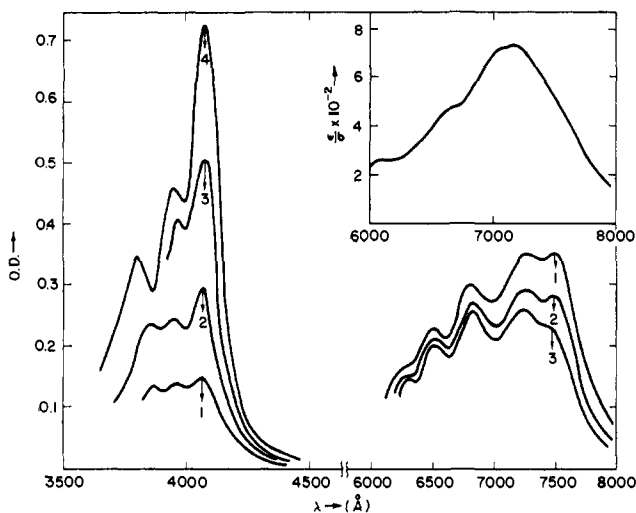


Fig. 1.—Absorption spectra of MTHF glasses containing 0.158 mole % biphenyl and  $x$  mole % anthracene: (1)  $x = 0.30$ ; (2)  $x = 0.15$ ; (3)  $x = 0.015$ ; and (4)  $x = 0$ . The spectrum of chemically prepared anthracene anion appears upper right, in terms of  $E/\sigma$ , where  $E$  is the molar extinction coefficient and  $\sigma$  is wave number (from ref. 2).

At this point, it is well to illustrate with a few examples the criteria which serve to characterize the anion spectra. Figure 1 represents the change in intensity of the authentic biphenyl anion spectrum<sup>7</sup> in juxtaposition to that of the anthracene anion and also, for comparison (upper right), the spectrum of the anthracene mononegative anion produced by chemical reduction.<sup>3</sup> First, the similarity of the spectrum of irradiated anthracene to that of the chemically prepared anion compels us to conclude that the mononegative ion is produced during  $\gamma$ -irradiation, and, second, the decrease of the biphenyl anion optical density with added anthracene validates the suggestion of a competitive process.

The negative triphenylethylene ion has not been reported thus far, but inspection of Fig. 2 shows that the band at approximately 5130 Å. must be attributed to triphenylethylene anion. The marked interdependence between the density of biphenyl anion absorption and this band cannot be explained otherwise.

In connection with Fig. 1 it is pertinent to make a few observations. The anthracene anion spectrum, in contrast to the majority of the spectra obtained, shows a marked vibrational structure consisting of five clearly resolved peaks and with an average separation of 675  $\text{cm}^{-1}$ .

The spectra of the "chemical" anion appears devoid of structure. This must surely be accounted for by the fact that the measurements were carried out at room temperature in liquid solutions. Also, the shifts of these anion band maxima (relative to the spectra of  $\gamma$ -irradiated samples) to shorter wave lengths must be attributed to the difference of the degree of association of the anions with the positive ions rather than with the solvent. Similar effects were observed in the spectra of phenanthrene, tetraphenylethylene, pyrene, 1,2-benzanthracene, triphenylene, and cycloheptatriene anions.

*o*-Terphenyl, on irradiation, produced a band at approximately 4300 Å. which has been identified as the anion absorption, and a weak absorption at approximately 6100 Å. Balk, *et al.*,<sup>3</sup> have reported two bands at 4500 and 8300 Å., respectively, for the mononegative ion, and an absorption at approximately 6500 Å. which

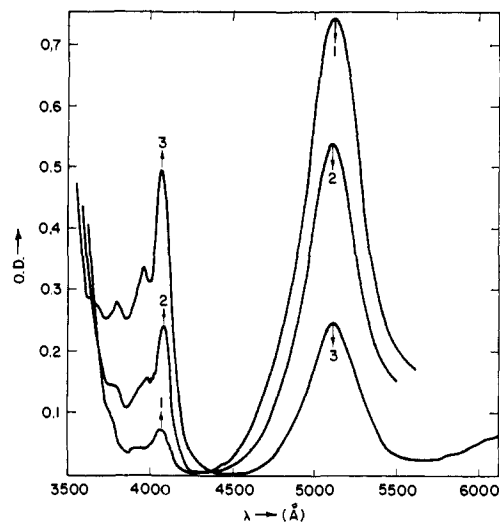


Fig. 2.—Absorption spectra of MTHF glasses containing 0.158 mole % biphenyl and  $x$  mole % triphenylethylene: (1)  $x = 0.20$ ; (2)  $x = 0.10$ ; and (3)  $x = 0.04$ .

they attributed to the binegative ion. These dissimilarities cannot be explained.

Triphenylene anion absorbed weakly from 6000 to 8000 Å. with peaks at 7650, 6850, 6550, and 6250 Å. (O.D. = 0.15, 0.17, 0.14, and 0.12, respectively) and also near 4100 Å. (O.D. = 0.35 at 4125 Å.). Solute concentration was 0.16 mole %. In mixtures with biphenyl, the O.D. at 4100 Å. decreased with increasing concentration of triphenylene and the determination of relative electron attachment efficiency was made on the basis of this variation.

1,2-Benzanthracene exhibits an anion absorption with a peak at approximately 4170 Å. For this reason, it was studied in competition with triphenylethylene rather than biphenyl.

Hexamethylbenzene (HMB) and cycloheptatriene were investigated in a mixture of 3MP-2MP-1 (3:1 by volume) prior to the selection of MTHF as a solvent. No distinguishable anion of HMB was observed, although in mixtures with biphenyl there was a concomitant reduction of the biphenyl anion optical density. This may be due to HMB anion absorption in the ultraviolet or far-ultraviolet region where its spectrum would be covered by the strong optical transition of the neutral molecule. In contrast, cycloheptatriene anion absorbs at approximately 4500 Å.

Columns B and C in Table I correspond to the hydrocarbon anions produced by reduction with sodium<sup>3</sup> and potassium,<sup>5</sup> respectively, under similar experimental conditions (*e.g.*, solvent, concentrations, etc.). It has been claimed<sup>5</sup> that anion bands lie at shorter wave lengths when potassium is used rather than sodium. If such an effect occurs, it is certainly very small and is contrary to what might be anticipated on the basis of the electrostatic interaction resulting from ion associations. Moreover, the fact that for a large number of organic-alkali metal systems in dilute solutions an appreciable red shift of the anion absorption maxima from lithium to cesium has been observed<sup>8</sup> suggests that the earlier observation (*cf.* ref. 5) may be incorrect.

The problem of the mechanism of anion formation has not been resolved thus far. It was expected on the

(8) (a) H. V. Carter, B. J. McClelland, and E. Warhurst, *Trans. Faraday Soc.*, **56**, 455 (1960); (b) B. J. McClelland, *ibid.*, **57**, 1458 (1961).

TABLE I  
POSITIONS OF THE ABSORPTION BANDS PRODUCED BY  $\gamma$ -IRRADIATION AND BY CHEMICAL REDUCTION

Hydrocarbon anion	Cm. <sup>-1</sup> × 10 <sup>4</sup>			Hydrocarbon anion	Cm. <sup>-1</sup> × 10 <sup>4</sup>			
	A <sup>a</sup>	B <sup>b</sup>	C <sup>c</sup>		A <sup>a</sup>	B <sup>b</sup>	C <sup>c</sup>	
Anthracene	13.3	14.0	13.8	Triphenylene	13.1	14.1	13.5	
	13.8		14.4		14.6	14.9	14.8	
	14.7	15.1	15.3		15.3			
	15.4		15.7		16.0	18.3	18.7	
	16.0	16.7	16.8		24.2	24.2	24.4	
		18.2	18.3		25.1			
Phenanthrene		24.9	24.8	1,2-Benzanthracene	24.0	28.8	29.0	
		15.3	15.7					
	22.4	22.5	22.4		<i>o</i> -Terphenyl	16.40	11.4	
	22.8						12.4	
	23.2						20.7	
24.0	24.1	24.1		21.4	21.2			
	25.3	26.4		23.5	22.3	22.6		
Pyrene		13.9	13.6	Triphenylethylene	19.5			
	15.2				Tetraphenylethylene	19.5		
	16.7							
	20.8	20.3	20.4					
	21.4							
	22.2	22.0	22.2					
23.6	26.0	26.1						
Biphenyl		27.3	27.5	Hexamethylbenzene	>25			
	26.3			Cycloheptatriene	22.0			
	25.2							
	24.6	24.7	24.9					

<sup>a</sup> Our results. <sup>b</sup> See ref. 3. <sup>c</sup> See ref. 5.

TABLE II  
COMPETITION OF 0.158 MOLE % BIPHENYL WITH ANTHRACENE AND TRIPHENYLETHYLENE IN MTHF AT -196° AND 0.75 × 10<sup>18</sup> E.V./ML.

Solute	Mole %	O.D., 4100 Å., biphenyl anion
None		0.76
Anthracene	0.075	0.50
Anthracene	0.150	0.29
Anthracene	0.300	0.15
Triphenylethylene	0.04	0.53
Triphenylethylene	0.10	0.24
Triphenylethylene	0.20	0.07

TABLE III  
RELATIVE ELECTRON ATTACHMENT EFFICIENCIES OF VARIOUS SOLUTES

Solute	Relative efficiency, $\sigma_s/\sigma_{\phi_1}$	$E$ , <sup>a</sup> volts	Molar refraction <sup>b</sup>
Biphenyl	1.00	0.00	52 <sup>c</sup>
Triphenylene	1.04	0.19	71
Phenanthrene	1.22	0.17	62 <sup>c</sup>
<i>o</i> -Terphenyl	1.40		74
Cycloheptatriene	1.94		30
Pyrene	1.95	0.60	67 <sup>c</sup>
Triphenylethylene	2.70		87
1,2-Benzanthracene	2.60	0.76	66
Tetraphenylethylene	2.76		118
Anthracene	2.76	0.78	65 <sup>c</sup>
Hexamethylbenzene	2.80		46

<sup>a</sup> Reduction potentials, expressed in volts against the reduction potential of biphenyl, are given by G. J. Hoijsink, E. de Boer, P. H. Van der Meij, and W. P. Weijland, *Rec. trav. chim.*, **75**, 487 (1956). <sup>b</sup> Molar refractions obtained by simple addition of bond refraction [Y. K. Syrkin and M. E. Dyatkina, "Structure of Molecules and the Chemical Bond," Butterworths, London, 1956]. <sup>c</sup> Corrected for refraction exaltation.

basis of simple considerations that the electron attachment efficiencies should increase with the size of the

molecules or the molecular polarizabilities. However, as can be seen in Table III, no such simple relationship exists. This is perhaps due to the fact that the incident electrons cannot modify to a significant degree the wave functions of the molecular electrons.

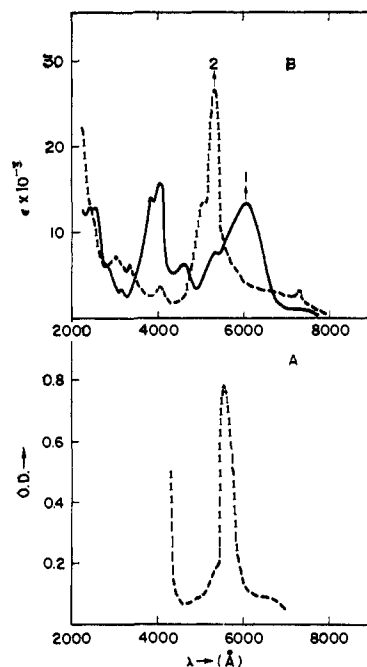


Fig. 3.—(A) Spectrum of  $\gamma$ -irradiated perylene in MTHF; (B) perylene in HF; (1) oxygen excluded; (2) contacted with oxygen (see ref. 11a).

On the other hand, it has been observed (*cf.* Table III) that  $\sigma_s/\sigma_{\phi_1}$  increases as the reduction potentials of hydrocarbons increase. But, in view of the fact that correlations between kinetic and thermodynamic quan-

tities are often difficult to justify theoretically this relationship should be accepted with a great many reservations, until further verifications are made.

Thus far, we have not mentioned the possibility of cation formation by  $\gamma$ -irradiation. On theoretical grounds one may expect monopositive and mononegative ions of alternant hydrocarbons to give similar electronic spectra.<sup>9</sup> We have, however, overlooked this possibility on the assumption that cation formation requires positive charge exchange between the solute and the molecules of the matrix. Since such an exchange is restricted in polar media, positive ion formation is expected to be limited.<sup>10</sup> In fact, this was found to be the case for all hydrocarbons except perylene. Perylene (*cf.* Fig. 3) exhibits an absorption at approximately 5800 Å. which is similar to that of the monopositive ion produced in oxygenated HF, CF<sub>3</sub>COOH + BF<sub>3</sub>·H<sub>2</sub>O, or concentrated H<sub>2</sub>SO<sub>4</sub>.<sup>11</sup> Not only that, but in solu-

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(10) J. P. Guarino and W. H. Hamill, *J. Am. Chem. Soc.*, **86**, 777 (1964).

(11) (a) G. Dallinga, E. L. Mackor, and A. A. V. Stuart, *Mol. Phys.*, **1**, 123 (1958); (b) W. I. Aalbersberg, G. J. Hoijsink, E. L. Mackor, and W. P. Weijland, *J. Chem. Soc.*, 3049 (1959).

tion with biphenyl its optical density increases slightly (but consistently) with added biphenyl. (At 0.079, 0.158, and 0.316 mole % biphenyl the optical density of 0.04 mole % irradiated perylene is 0.68, 0.75, and 0.81, respectively.) This change in optical density cannot be explained by anion or free-radical formation. Neither can this be accounted for by formation of perylene-proton complex, since such a complex gives an entirely different spectrum.<sup>11</sup> It must, therefore, be attributed to the positive ion of perylene. This is consistent with the observation that perylene, compared with other aromatic hydrocarbons, in concentrated H<sub>2</sub>SO<sub>4</sub> or CF<sub>3</sub>COOH + BF<sub>3</sub>·H<sub>2</sub>O solutions, easily forms the monopositive ion. However, the over-all yield,  $G$  (perylene<sup>+</sup>) = 2.51,<sup>12</sup> of perylene positive ion is remarkably large for a solute at low concentration in a polar solvent and the assignment is tentative.

**Acknowledgment.**—We thank Professor John L. Magee and Dr. Paul Funabashi for useful discussions.

(12) The yield was calculated on the basis of an absorption coefficient of  $2.68 \times 10^4$  taken from the data of ref. 11a.

[CONTRIBUTION FROM THE STANFORD RESEARCH INSTITUTE, MENLO PARK, CALIFORNIA]

## Iodine-Catalyzed Isomerization of Olefins. I. Thermodynamic Data from Equilibrium Studies of Positional and Geometrical Isomerization of 1-Butene and 2-Butene

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The kinetics and thermodynamics of the iodine atom catalyzed positional and geometrical isomerization of 1-butene and 2-butene have been studied. In this paper, first of a series, equilibrium constants ( $K$ ) for the reactions 1-butene  $\xrightleftharpoons[k_4]{k_3}$  *trans*-2-butene and *cis*-2-butene  $\xrightleftharpoons[k_6]{k_5}$  *trans*-2-butene are reported. The  $K_{3,4}$  values, measured over a wider temperature range (192 to 332°) and with greater precision than had been done earlier,<sup>1</sup> lead to  $\Delta H^\circ_{3,4} = -2.8 \pm 0.2$  kcal./mole and  $\Delta S^\circ_{3,4} = -3.1 \pm 0.4$  e.u. These values are to be compared with the less reliable data from the API tables of  $-2.6$  kcal./mole and  $-2.1$  e.u., respectively. The  $\Delta H^\circ_{5,6}$  and  $\Delta S^\circ_{5,6}$  calculated from  $K_{5,6}$  values (87 to 332°) differ from the API data by about 0.4 kcal./mole and 0.7 e.u., respectively. As anticipated, minor amounts of butadiene and *n*-butane are observed.

### Introduction

Recently Benson and co-workers<sup>1a,1b</sup> showed that in a temperature range of 200–300° catalytic amounts of iodine vapor bring about quite rapid positional as well as geometrical isomerization of olefins. Measurement of the equilibrium constants from the iodine-catalyzed reaction of olefins and their parent hydrocarbons constitutes a very valuable tool for the precise measurement of the differences in the thermodynamic properties of the reactants. Applied to the butene isomerization Benson and Bose<sup>1a</sup> obtained for the positional isomerization values for  $\Delta H^\circ$  and  $\Delta S^\circ$  that disagreed by about 0.5 kcal./mole and 1.6 e.u., respectively, with the data from the API tables.<sup>2</sup> For the geometrical

isomerization the agreement with API was excellent. The new measurements reported here were aimed at examining these differences more carefully.

Because of the absence of appreciable side reactions and the simplicity of the mechanism of iodine atom attack on olefins, the method is extremely well-adapted for studying resonance effects as well as precise thermodynamic data; toward these ends, we have begun a program of investigation into the kinetics of isomerization of simple and conjugated olefins. The present paper reports measurements of the equilibrium constants for the positional and geometrical isomerization of 2-butene and 1-butene.<sup>1c</sup>

### Experimental

The experimental procedure described herein is applicable to both equilibrium and kinetic measurements.

(a) **Materials.**—Research grade butene isomers were supplied by the Phillips Petroleum Company and were further purified by distillation under vacuum. They were stored in large glass bulbs connected to a standard-type gas handling and vacuum system. G.l.c. (gas-liquid chromatography) analysis showed less than  $10^{-3}$  mole % impurities. Reagent grade resublimed iodine was used.

(1) (a) S. W. Benson and A. N. Bose, *J. Am. Chem. Soc.*, **85**, 1385 (1963). (b) S. W. Benson, A. N. Bose, and P. Nangia, *ibid.*, **85**, 1388 (1963). (c) Subsequent papers will discuss the kinetics of the positional isomerization involving the allylic resonance in the butenyl radical and the kinetics of the *cis-trans* isomerization of 2-butene which involves the addition of the iodine atom to the double bond and the rate-controlling step of rotation of the ethylenic radical around a single bond.

(2) "Selected Values of Physical and Thermodynamic Properties of Hydrocarbons and Related Compounds," American Petroleum Institute, Carnegie Press, Pittsburgh, Pa., 1953.