Ultraviolet Absorption Spectra of Phenanthrene in Various Solvents

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These can easily be solved by differentiating (a) and substituting in the resultant equation for dy/dt from (b). We thus obtain:

$$\frac{d^2x}{dt^2}+2k_1\frac{dx}{dt}+2k_1\cdot k_2\cdot x=0,$$

and the initial conditions are that for $t=0$, $x=0$, and $dx/dt=2k_1\cdot C_0$. Since our initial assumption was that $k_2>k_1$, the discriminant $k_1^2-2k_1k_2$ is negative and, therefore, the solution has a form similar to that obtained for a damped oscillator

$$x=2k_1\cdot c_0/\alpha\cdot e^{-k_1\cdot t}\cdot\sin\cdot(\alpha\cdot t),$$

where $\alpha^2=2k_1\cdot k_2-k_1^2$.

The solution for y is obtained by simple integration:

$$y=c_0-c_0/\alpha\cdot(2k_1\cdot k_2)^{\frac{1}{2}}\cdot e^{-k_1 t}\cdot\sin\cdot(\alpha\cdot t+\vartheta),$$

where

$$\sin\vartheta=\alpha/(2k_1\cdot k_2)^{\frac{1}{2}}.$$

As can easily be verified, both y and dy/dt are 0 for $t=0$. Therefore, for very small values of t, y is given by the square term of Taylor's series, i.e.,

$$y\sim\frac{1}{2}\left(\frac{d^2y}{dt^2}\right)_{t=0}\cdot t^2=k_1\cdot k_2\cdot c_0\cdot t^2.$$

The appearance of the trigonometric functions in chemical kinetics is rather unusual. It should be noted, however, that since obviously $x+y$ cannot be greater than C_0 the expressions given above break down at a time $t_f<\pi/2\alpha$, i.e., before $\sin(\alpha\cdot t)$ reaches its maximum value of 1.

* I am indebted to Professor C. E. H. Bawn for this information.
** The factor 2 arises from reaction (3) which produces allyl radicals from H atoms formed in reaction (1).
[1] M. Polanyi and E. Wigner, Zeits. f. physik Chemie A139, 439 (1928).
[2] See Glasstone, Laidler, and Eyring, *The Theory of Rate Processes; The Kinetics of Chemical Reactions, Viscosity, Diffusion and Electrochemical Phenomena* (McGraw-Hill Book Company, Inc., New York, 1941).
[3] Ziegler, Orth, and Weber, Annalen 504, 131 (1933); Ziegler, Leib, Kuoevangel, and Anders, *ibid.* 551, 161 (1942); E. T. Butler and M. Polanyi, Trans. Faraday Soc. 39, 19 (1943); M. Szwarc, J. Chem. Phys. 16, 128 (1947); and the following papers.
[4] M. Szwarc, J. Chem. Phys. (in press).

Ultraviolet Absorption Spectra of Phenanthrene in Various Solvents.

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IN a recent letter Vodar and Robin[1] described the ultraviolet absorption spectra of phenanthrene dissolved in compressed gases (nitrogen and argon). They illustrate in the case of argon at constant temperature the displacement of the absorption bands as a function of the density of solvent, showing a red shift with increasing density.

As part of a comprehensive program[2] on the ultraviolet absorption spectra of aromatic hydrocarbons, we examined phenanthrene[3] in various solvents (iso-octane, ethyl alcohol, chloroform, and benzene) with the interesting result at room temperature of displacements of the absorption bands (predominantly red shifts when using iso-octane as the reference solvent) of pronounced regularity (Fig. 1), and also of characteristic changes in the absorp-
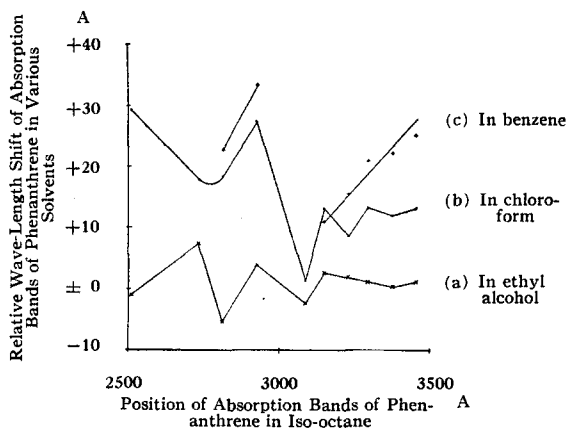

FIG. 1.

tion intensities (expressed as $\Delta(\log_{10}\epsilon)$, where ϵ = molecular extinction coefficient) of the various bands (Fig. 2).

In agreement with the results obtained on other aromatic hydrocarbons,[4] and in particular with the still more regular wave-length shifts in the absorption spectra of anthracene, there is no clear hint of the connection of this definitely existing solvent effect (even in cases where there is no chemical reaction taking place between the solute and the solvent) either with the dipole moment, or the refractive index, or the density of the solvent.

In the present case the concentration of the phenanthrene solutions in iso-octane was 1 part in 272,440 by weight for the measurement of the short wave-length end of the spectrum, and 1 part in 1308 by weight for the long wave-length end. The accuracy of the wave-length determination of the absorption peaks is within $\pm4A$, and the absorption intensities are determined to about ±5 percent. It appears from Fig. 1 that the red shift at the long wave-length end of the spectrum is very small in ethyl alcohol, whereas it is considerable in chloroform and still larger in benzene. Table I shows that the distances between neighboring absorption bands are very similar in the four solvents except for bands A^5 and D, both of which exhibit a large red shift in chloroform and therefore give compara-
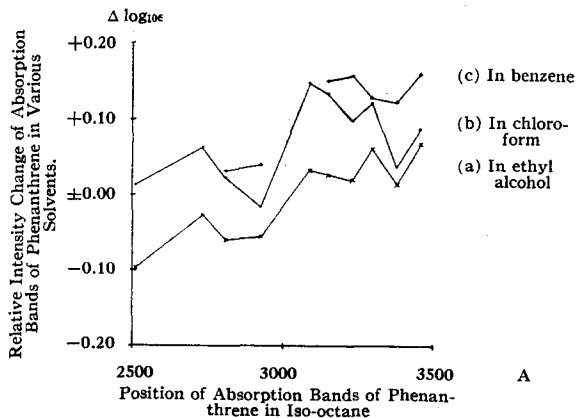

FIG. 2.

TABLE I. Distances between neighboring absorption bands in A.

Solvent	Distance between adjacent bands								
	A–B	B–C	C–D	D–E	E–F	F–G	G–H	H–I	I–J
Iso-octane	223	78	114	161	62	80	66	83	78
Ethyl alcohol	232	65	124	155	67	80	65	82	79
Chloroform	212	78	123	135	74	76	71	82	79
Benzene	—	—	125	—	—	85	71	84	81

tively smaller distances from their long wave-length neighbors.

Of some interest is also the *percentage* change in absorption intensity on passing from iso-octane to one of the other three solvents. All three give rise to an increase in absorption intensity at the long wave-length end of the spectrum (Table II), and only ethyl alcohol seems to weaken the absorption at the short wave-length end.

TABLE II. Percentage change of absorption intensity in the ultra-violet spectrum of phenanthrene in various solvents both below and above 3000A as compared to phenanthrene in iso-octane.

Solvent	Maximum percentage change of absorption	
	below 3000A	above
Ethyl alcohol	−6 to −20	+3.5 to +17
Chloroform	−3.5 to +15.5	+9.1 to +40.4
Benzene	+9.5 to +10.1	+32.3 to +45

[1] B. Vodar and S. Robin, J. Chem. Phys. **16**, 996 (1948).
[2] R. Schnurmann and S. Whincup, Petroleum **8**, 122 (1945).
[3] We are indebted to Dr. M. Sulzbacher of the Grosvenor Laboratory, London, for the synthesis of this particular sample of phenanthrene.
[4] A detailed account of this work will be published elsewhere.
[5] The phenanthrene bands are here lettered alphabetically beginning with A at the short wave-length end of the spectrum.

An Effect of Isotopic Mass on the Rate of a Reaction Involving the Carbon-Carbon Bond*

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INVESTIGATION on the effect of the difference in mass between isotopes upon the rate of a chemical transformation has been limited entirely to the very lightest of the elements, especially hydrogen, although the effect of isotopic mass upon the rate of many physical processes has been extended throughout the periodic table.[1] The effect of isotopic mass on certain chemical equilibria has been used to separate the isotopes of carbon and nitrogen. Recently, the isotope effect on the rate of a chemical reaction has been observed by Beeck[2] who demonstrated in the course of a study of the isomerization of propane that the dissociation probability of the $C^{12}-C^{12}$ bond was increased 77 percent, and that of the $C^{13}-C^{12}$ bond decreased 12 percent from the dissociation probability of the $C^{12}-C^{12}$ bond in unlabeled propane. Further experiments[3] by the same authors yield a $C^{12}-C^{12}/C^{13}-C^{12}$ rupture ratio of 1.08 for thermal cracking at 500°, contrasted with 1.22 for electron impact rupture.

Decarboxylation reactions can be made to take place at moderate temperatures, and for a given reaction the isotope effect should increase with decreasing temperature. If a symmetrical dicarboxylic acid, labeled in only one carboxyl group, is decomposed to form a monocarboxylic acid and carbon dioxide, the primary competition for reaction is between the different functional groups in the same molecule. Assuming the same type of bond strengthening and weakening noted above, the carbon dioxide evolved would be impoverished in the label, while the mono-acid produced would be similarly enriched in label. Since the isotopic constitution of the remaining di-acid is unaffected, this result of symmetry can be used to "retire" part of the "chemically active" label and produce a level rate of isotope label enhancement with a constant net effect at any stage of the decarboxylation process.

Singly labeled malonic acid was prepared from chloracetic acid and active cyanide after the procedure of Weiner.[4] The product was recrystallized from diethyl ether—60° petroleum ether mixtures; m.p. 135°. A part of this acid was treated with bromine in moist ether, and the bromomalonic acid formed recrystallized from acetone and benzene. (The bromomalonic acid finally employed was not of great purity.)

A few hundred mg of acid was placed in the bottom of a pear-shaped flask, which could be swept throughout with nitrogen. The flask was heated in an oil bath ~10° above the decomposition temperature of the acid; carbon dioxide was swept through dry-ice-acetone traps (which served to collect much of the product mono-acid) into sodium hydroxide-filled absorption bubblers. After apparent completion of the reaction, the mono-acid was transferred to a combustion train. Two malonic acid experiments were performed, using 6 and 10 moles, respectively; one 2.1 mole bromomalonic acid decarboxylation was carried out.

The results of the experiments are shown in Table I. The frequency of rupture ratios was obtained by pairing each of the specific activity figures with those remaining, and the approach to identity of the three quotients thus obtained is a measure of the internal consistency of the experimentally derived data. The three bases noted are: A, carbon dioxide and di-acid; B, mono-acid and di-acid; C, carbon dioxide and mono-acid.

It is to be noted that the above ratios, that is 1.12 for malonic acid and 1.4 for the bromomalonic, are considerably larger than any isotope effects that have been observed in chemical equilibria. It is, of course, to be expected that the effect of the zero-point energy difference on a chemical rate process should be larger than its effect on an

TABLE I.

Compound	F_{12-12} basis B	F_{12-14} basis A	F_{12-12}/F_{12-14} basis		
			A	B	C
Malonic acid	0.531 ±0.016	0.474 ±0.015	1.13 ±0.03	1.11 ±0.03	1.12 ±0.03
Bromo-malonic acid	0.61 ±0.04	0.44 ±0.03	1.30 ±0.11	1.57 ±0.15	1.41 ±0.08