be considered an exception, even though its rate constant is not far from the expected value. For this acid, both the inductive effect of the phenyl group and the influence of substitution are outweighed by resonance between the carboxyl and phenyl groups. This causes the slow rate of esterification and high activation energy found with this acid.

4. The relatively fast rate for cyclohexanecarboxylic acid is apparently due to the lack of freedom of the β-carbon atoms to be oriented toward the carboxyl group. This has been previously discussed.[12]

In general, activation energies show an increase with decreasing rate constants, this effect being negligible until three or more substitutions are present.

Summary

The kinetics of the acid catalyzed esterification of the following organic acids have been studied: cyclohexylacetic, β-cyclohexylpropionic, γ-cyclohexylbutyric, dicyclohexylacetic, phenylethylacetic, δ-phenylvaleric, diphenylacetic, and triphenylacetic acids.

It is demonstrated that, in general, the rate of esterification of such organic acids is governed primarily by the total number of substitutions in the α- or β-positions. Exceptions may be caused by such complicating factors as multiple α-substitution, resonance, the inductive effect of an α-phenyl group, and joining of the β carbon atoms.

KNOXVILLE, TENNESSEE RECEIVED JUNE 9, 1944

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[12] Smith and Levenson, THIS JOURNAL, 62, 2733 (1940).

[JOINT CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AND THE COAL RESEARCH LABORATORY, CARNEGIE INSTITUTE OF TECHNOLOGY]

The Ultraviolet Absorption Spectra of Hydrocarbon–Trinitrobenzene Complexes

BY R. C. JONES AND M. B. NEUWORTH

The identification of aromatic hydrocarbons from their ultraviolet absorption spectra has been well established. Since the substitution of an alkyl group or an alicyclic ring does not alter significantly the spectrum of the aromatic ring system, ultraviolet absorption spectra have become a valuable identification tool.[1]

The ability of aromatic hydrocarbons to form crystalline complexes with polynitro compounds is a very useful property. These complexes permit purification, separation of mixtures, and serve as crystalline derivatives. This is particularly advantageous when the hydrocarbons are liquids or difficultly crystallizable oils.[2] The direct interpretation of the spectrum of a hydrocarbon–polynitro complex would, therefore, be a convenient technique.

The ultraviolet absorption spectra were determined for the symmetrical trinitrobenzene complexes of naphthalene, anthracene, phenanthrene, pyrene, chrysene, 1,2-benzopyrene, and 1,2,5,6-dibenzanthracene. At the concentration employed for the spectrum analysis (10^{-3} molar maximum concentration) in methanol, it was found that the complexes were completely dissociated.[3] The absorption curve was the sum of the absorption of the hydrocarbon and the trinitrobenzene. This was substantiated in all cases by adding the molar extinction coefficients of the hydrocarbon and the trinitrobenzene at a given wave length, and comparing the sum with the experimental molar extinction coefficient of the complex. Fortunately, for all ring systems except naphthalene, the hydrocarbon absorption is sufficiently higher than the trinitrobenzene for most of the spectrum so as to enable direct identification of the aromatic ring system without the necessity of calculating the trinitrobenzene absorption.

Preliminary experiments with picrates indicated undesirable complications existed. When pyrene picrate was studied in methanol, it became obvious on examination of the spectrum that the picric acid was almost completely ionized. The picrate ion has a very high absorption[4] and tends to mask a considerable portion of the fine structure of the hydrocarbon. Attempts to eliminate the ionization by an increase in acidity of the solvent were unsuccessful. This is not a serious drawback since symmetrical trinitrobenzene forms more stable complexes with aromatic hydrocarbons than picric acid.

In Fig. 1 the ultraviolet absorption spectra of naphthalene and trinitrobenzene are indicated. The spectrum of naphthalene–trinitrobenzene complex is included superimposed on the calculated curve obtained by adding the molar extinction coefficients for naphthalene and trinitrobenzene at each wave length and plotting the logarithm of the sum against the wave length of light. Deviations of the experimental curve from the calculated curve are indicated by a dotted line.

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[1] R. N. Jones, *Chem. Rev.*, 32, 1 (1943).

[2] C. K. Bradsher and L. Rapoport, THIS JOURNAL, 65, 1646 (1943); F. Bergmann and H. E. Eschinazi, *ibid.*, 66, 183 (1944).

[3] This is in agreement with the dissociation constants of acenaphthene–trinitrobenzene and acenaphthene–picric acid which have been determined spectrographically (H. von Halban and E. Zinpelmann, *Z. physik. Chem.*, 117, 461 (1925)). A spectroscopic analysis of the desoxycholic acid complexes of methylcholanthrene and 1,2,5,6-dibenzanthracene showed complete dissociation of the complex in dilute ethanol and ether solutions (L. F. Fieser and M. S. Newman, THIS JOURNAL, 57, 1603 (1935)).

[4] P. Gross, A. Jamok and F. Batat, *Monatsh.*, 63, 117 (1933).

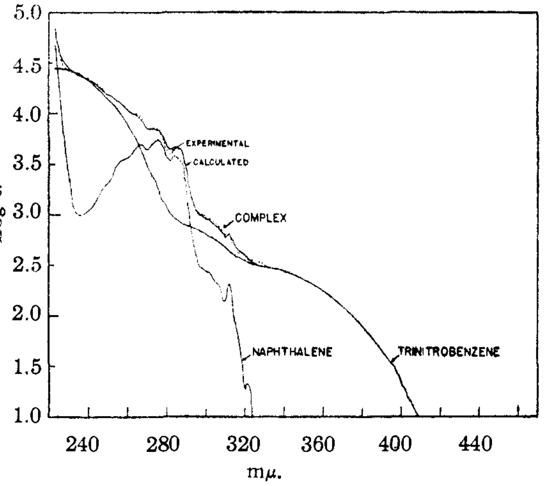

Fig. 1.

In Figs. 2, 3 and 4 the spectra of the trinitrobenzene complexes of anthracene, phenanthrene, pyrene, chrysene, 1,2-benzopyrene, and 1,2,5,6-dibenzanthracene are indicated compared with the spectra of the free hydrocarbons. 1,2,5,6-Dibenzanthracene forms a complex with two moles of trinitrobenzene. A dipicrate had been isolated previously.[5] The ease with which the hydrocarbon-trinitrobenzene spectra can be interpreted is obvious upon examination of Figs. 2, 3 and 4.

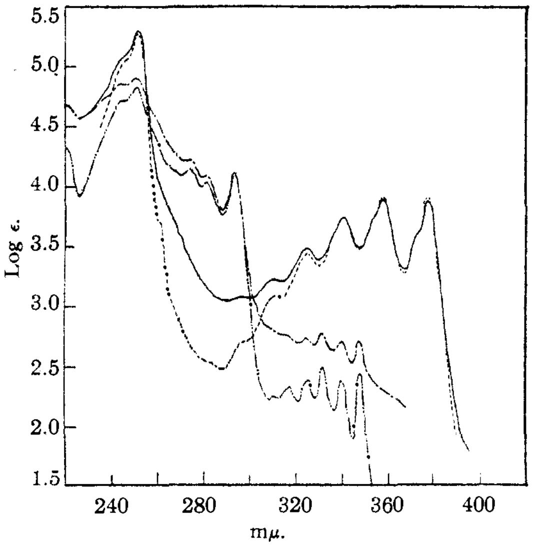

Fig. 2.——— Anthracene-trinitrobenzene; - - - - - anthracene; — — — — — phenanthrene-trinitrobenzene; — · · — · · phenanthrene.

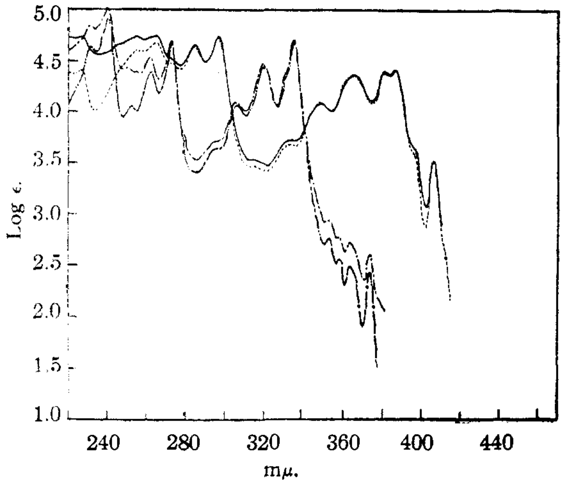

Fig. 3.— ——— 1,2-Benzopyrene-trinitrobenzene; - - - - - - 1,2-benzopyrene; — — — — pyrene-trinitrobenzene; — · · — · · pyrene.

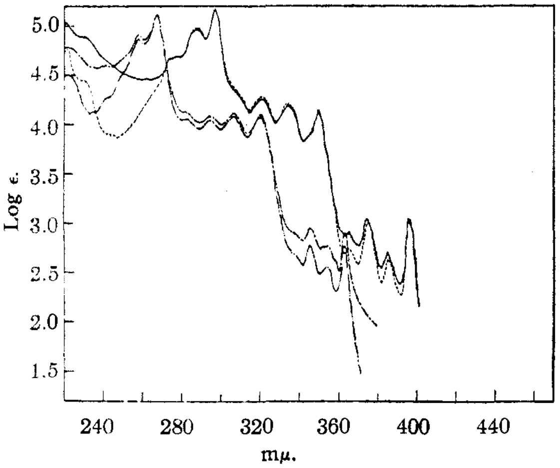

Fig. 4.— ——— 1,2,5,6-Dibenzanthracene-trinitrobenzene; - - - - - - 1,2,5,6-dibenzanthracene; — — — — — chrysene-trinitrobenzene; — · · — · · chrysene.

In Table I the experimental molar extinction coefficients of the maxima for the hydrocarbon-trinitrobenzene complexes are compared with the molar extinction coefficients calculated by adding the molar extinction coefficients of the hydrocarbon and the trinitrobenzene at a given wave length.[6]

Since it is possible to obtain an ultraviolet absorption spectrum with a few milligrams of material, this technique may be considered a micro identification tool.

Experimental

All spectra were obtained on a Beckman photoelectric spectrophotometer. Readings were taken at 1 mμ intervals. Samples were weighed out on a micro balance. Analytical reagent, acetone-free absolute methanol was used in all cases.

Materials.—All hydrocarbons except naphthalene were purified through the trinitrobenzene complex. The complexes were broken down and

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(5) R. Weitzenböck and A. Klinger, *Monatsh.*, **39**, 315 (1918).

(6) In the case of 1,2,5,6-dibenzanthracene the calculated extinction coefficient is obtained by adding the molar extinction coefficient of the hydrocarbon to twice the molar extinction coefficient of trinitrobenzene.

the hydrocarbon recovered by passing a solution of the complex in petroleum ether–benzene through a column packed with activated alumina-Super-Cel. The recovered hydrocarbon was then crystallized from a suitable solvent. The naphthalene was recrystallized from methanol–water (Bureau of Standards sample for calorimetric work). The trinitrobenzene was decolorized with charcoal and recrystallized twice from methanol–water (m. p. 124.3–124.8° cor.). In Table II the melting points of the hydrocarbons and the trinitrobenzene complexes are listed,

TABLE I

Pyrene–T. N. B.

mμ	Log ε Calcd.	Log ε Exp.
231	4.84	4.84
240	5.01	5.02
252	4.38	4.39
262	4.49	4.51
273	4.68	4.69
295	3.70	3.70
306	4.08	4.09
320	4.44	4.46
335	4.69	4.70
353	2.90	2.90
358	2.74	2.75
364	2.67	2.66
374	2.57	2.58

1,2,5,6-Dibenzanthracene–T. N. B.

mμ	Log ε Calcd.	Log ε Exp.
221	5.05	5.03
278	4.71	4.68
288	4.98	4.95
297	5.17	5.16
321	4.27	4.25
334	4.21	4.19
350	4.16	4.13
365	2.92	2.91
375	3.08	3.05
385	2.73	2.71
396	3.06	3.03

Anthracene–T. N. B.

mμ	Log ε Calcd.	Log ε Exp.
252	5.29	5.30
298	3.07	3.08
311	3.23	3.23
325	3.49	3.49
340	3.92	3.90
358	3.90	3.87
378	3.76	3.74

1,2-Benzopyrene–T. N. B.

mμ	Log ε Calcd.	Log ε Exp.
226	4.73	4.73
255	4.70	4.73
264	4.72	4.74
284	4.64	4.66
296	4.73	4.74
332	3.70	3.71
348	4.09	4.08
366	4.37	4.36
380	4.39	4.39
386	4.42	4.41
406	3.51	3.52

Chrysene–T. N. B.

mμ	Log ε Calcd.	Log ε Exp.
242	4.59	4.60
258	4.91	4.91
267	5.11	5.11
295	4.07	4.09
307	4.10	4.11
320	4.09	4.10
345	2.93	2.94
354	2.75	2.77
363	2.87	2.88

Phenanthrene–T. N. B.

mμ	Log ε Calcd.	Log ε Exp.
244	4.85	4.86
251	4.91	4.91
274	4.21	4.22
281	4.08	4.10
293	4.14	4.11
309	2.83	2.82
316	2.77	2.76
324	2.76	2.74
331	2.79	2.78
339	2.72	2.71
347	2.71	2.72

TABLE II

Hydrocarbon	m. p. °C. (cor.)	Trinitrobenzene complex, m. p. °C. (cor.)
Naphthalene	81–81.8	155.2–155.8
Phenanthrene	100.8–101.3	165.8–166.4
Anthracene	216.5–217.2	163–164
Pyrene	152.2–152.9	252.5–253.3
Chrysene	255.8–256.3	188.5–189.5
1,2-Benzopyrene	179.9–180.3	227–228.5
1,2,5,6-Dibenzanthracene	269–270	237.0–238.5[7]

Acknowledgment.—The authors wish to acknowledge the assistance of Miss F. A. Lawrence and C. L. McCabe in carrying out the spectra determinations.

Summary

Ultraviolet absorption spectra of dilute methanol solutions of aromatic hydrocarbon–trinitrobenzene complexes have demonstrated the complete dissociation of the complex. The concept of complete dissociation and the additivity of spectra has been applied to representative two, three, four, and five ring hydrocarbons. The application of this concept as an identification tool has been pointed out.

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(7) Calculated for $C_{22}H_{14}\cdot 2C_6H_3N_3O_6$: C, 57.96; H, 2.86. Found: C, 57.50; H, 2.74.

PITTSBURGH, PENNSYLVANIA RECEIVED JUNE 12, 1944

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, NORTHWESTERN UNIVERSITY MEDICAL SCHOOL]

Adsorption of Water Vapor by Proteins[1]

BY HENRY B. BULL

Many workers have concerned themselves with the combination between water and proteins and the present author cannot lay claim to originality in either his belief in the importance of the problem or in his approach to the subject. He has, however, been somewhat more persistent than most and has arrived at certain conclusions which seem to warrant publication at this time.

As pointed out by Sponsler, Bath and Ellis,[1a] proteins contain two types of hydrophilic groups which are capable of binding water through hydrogen bond formation. These are the polar side chains such as those from lysine, glutamic acid, tyrosine, etc., and, second, the oxygen and nitrogen associated with the peptide bonds in the peptide chains. The amount of water held by a protein should be primarily determined by the number and availability of these two types of groups.

Previous work on the adsorption of water vapor by proteins such as that reported by Briggs,[2] shows quite clearly that a typical S-shaped curve is obtained when the amount of water vapor adsorbed is plotted against the relative humidity. This characteristic adsorption curve can be

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[1] This paper was presented at the Cleveland, Ohio, meeting of the American Chemical Society, April 5, 1944.

[1a] Sponsler, Bath and Ellis, *J. Phys. Chem.*, **44**, 996 (1940).

[2] Briggs, *J. Phys. Chem.*, **35**, 2914 (1931); **36**, 367 (1932).