These observations again emphasize that viscosity is not a sufficient criterion for predicting the behavior of molecules. Viscosity depends on the interaction of solvent molecules with each other and the very viscous solvents contain large molecules that interfere with each other's motions. The iodine atoms are much smaller than the solvent molecules. Viscosity should vary approximately as the square of molecular complexity but the ability of an atom to move through the medium should depend more nearly on the first power of this complexity. Although these ideas are very crudely expressed, they rationalize the observation that increasing viscosity increases the factor by which the observed quantum yield exceeds the value calculated by Method I.

(3) *The quantum yields in viscous solvents approach a limiting value that is not reduced by further increases in viscosity.* Although Method II can be made to reproduce this effect, it does so only by means of an *ad hoc* assumption that is inconsistent with the idea of a viscous solvent continuum as used in the rest of the derivation; in fact, the assumption of Method II is tantamount to postulating that the observed effect does exist!

If quantum yields in USP 335 were measured at longer wave lengths, Method I predicts that the value for red light should fall to well below 0.01, while Method II predicts that it should remain about 0.036. Our experience with other solvents[8] makes us feel that the assumption of Method II would be rejected if this experimental test were performed.

If the assumption of Method II can indeed be rejected, the observed limiting quantum yield is in direct violation of the predictions of the theory based on the solvent as a viscous continuum. The observations are more consistent with the original "cage" picture of Rabinowitch[10] in which the separating atoms are held together by specific solvent molecules. As the molecular weight of hydrocarbons increases, a situation is reached where the iodine atoms are effectively pushing against only a few segments of molecules rather than against the molecules as a whole. Escape of iodine atoms will then take place only if the direction of recoil is such as to permit an atom to force its way between two adjacent molecules and the probability of escape will be almost independent of the sizes and complexities of the parts of each solvent molecule that were not directly affected. Beyond a certain limit, increases in molecular complexity will increase viscosity but will be virtually without influence on quantum yield. Such an interpretation would require preservation of the distinction between "primary" and "secondary" recombination,[11] while models regarding the solvent as a continuum do not need to make this distinction.

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[10] E. Rabinowitch and W. C. Wood, *Trans. Faraday Soc.*, **32**, 1381 (1936).

[11] R. M. Noyes, THIS JOURNAL, **77**, 2042 (1955).

EUGENE, OREGON

[CONTRIBUTION FROM THE CHANDLER LABORATORY OF COLUMBIA UNIVERSITY AND FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF OREGON]

The Dependence on Wave Length of Quantum Yields for Iodine Dissociation

BY LENORE F. MEADOWS[1] AND RICHARD M. NOYES[2]

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Quantum yields for iodine dissociation have been measured at 25° in hexane and in hexachlorobutadiene-1,3 for six wave lengths from 4047 to 7350 Å. For these wave lengths, the initial kinetic energies divided between the separating atoms ranged from 35.0 to 3.3 kcal./mole. Quantum yields at 4358 A. are in fair agreement with values predicted by a theory that treats the surrounding solvent as a viscous continuum and that uses no parameters not capable of independent measurement; the quantum yields at 7350 Å. are in good agreement with the predictions of the same theory for eventual separation of two atoms starting apart with only thermal kinetic energies. However, the quantum yields at intermediate wave lengths fail to reproduce the pattern predicted by the theory. The discrepancies directly support a proposal originally made by Rabinowitch that solvent molecules push together two atoms separated by less than a certain critical distance but that the solvent molecules preferentially push apart atoms separated by a little more than this critical distance. The data also suggest that for atoms separating with kinetic energies of only a few kcal./mole the probability of escape is much more dependent on the chance distribution of solvent molecules in space than it is on the absolute value of this small kinetic energy of separation. Any further quantitative theoretical advance must specifically recognize the discrete molecular nature of the solvent.

Introduction

This study is part of a program to learn more about molecular interactions in liquids by measuring quantum yields for iodine dissociation under a variety of conditions. When the molecule absorbs a quantum containing more than enough energy to break the bond, the excess appears as kinetic

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[1] Based on the Ph.D. Dissertation of Lenore F. Meadows. The original dissertation and microfilms thereof are available from the Library of Columbia University, New York, N. Y.

[2] To whom inquiries should be sent: Department of Chemistry, University of Oregon, Eugene, Oregon.

energy of the separating atoms. They rapidly lose this kinetic energy and then have a finite probability of recombining during subsequent diffusion. This probability depends on the nature of the solvent and on the separation attained before the excess kinetic energy is dissipated.

We have already measured quantum yields at a single wave length[3] in solvents whose relative viscosities covered a range of 10^3; for two solvents of low viscosity we have now measured quantum yields over a range of wave lengths such that the kinetic energies of the separating atoms varied from 3.3 to 35.0 kcal./mole.

If an illuminated solution of iodine undergoes no net chemical change, the photostationary state is described by the expression

$$I = (\phi q/k)^{1/2} \qquad (1)$$

where I = photostationary concentration of iodine atoms
ϕ = quantum yield for production of atoms that escape their original partners
q = rate of absorption of quanta per unit volume
k = rate constant for combination of atoms that have escaped their original partners

The isotopic exchange of elementary iodine with *trans*-diiodoethylene involves iodine atoms but not molecules,[4] so

$$R = k_e I b \qquad (2)$$

where R = rate of isotopic exchange
k_e = rate constant for exchange of iodine atoms with diiodoethylene molecules
b = concentration of diiodoethylene

Since the rate constants k and k_e depend on solvent and temperature but are presumably independent of the wave length of the initiating light, it follows from equations 1 and 2 that

$$\phi_B = \phi_A \frac{q_A b_A^2 R_B^2}{q_B b_B^2 R_A^2} \qquad (3)$$

where the subscripts A and B refer to two different wave lengths for illumination of the same solvent.

Since absolute quantum yields at 4358 Å. and 25° already have been measured in some solvents by a scavenger technique,[5] quantum yields at other wave lengths in these solvents could be calculated from equation 3 if rates of exchange were measured at known intensities of illumination provided one of the wave lengths were 4358 Å.

Experimental

Materials.—Two solvents were used. Hexane was prepared from commercial grade 65–70° petroleum ether by repeated stirring with 20% fuming sulfuric acid, followed by treatment with acid permanganate and then sodium carbonate solutions. It was distilled and stored over sodium. Commercial hexachlorobutadiene-1,3 was vacuum distilled and the fraction boiling in the range 75–80° at 5 mm. was used. Both solvents contained impurities capable of reacting with about 3×10^{-6} mole/l. of iodine.

The *trans*-diiodoethylene had been prepared previously in these Laboratories.[6] Solutions were prepared by direct weighing.

Resublimed C.P. grade iodine was used without further purification. Solutions in the different solvents were activated by shaking with aqueous solutions of carrier-free iodine-131 from the U. S. Atomic Energy Commission. Concentrations were determined spectrophotometrically.

Apparatus.—Reactions were carried out at 25° in cylindrical cells 2.00 cm. long and 1.70 cm. in diameter fitted with side arms to contain the solution while it was being frozen and degassed. Quantities of solution were chosen so as just to fill the cylindrical portions of the cells. During a run, the cell was mounted on an optical bench in a chamber through which thermostated water was pumped. Windows in the chamber permitted illumination.

Each experiment involved illumination at one of six wave lengths. The 4047, 4358, 5461 and 5790 Å. lines were isolated from a thermostated mercury AH4 arc by means of appropriate filters. Illumination at 6430 or 7350 Å. was obtained with a Fabry-Perot type narrow band interference filter in front of a 500 watt tungsten filament projection lamp.

The light beam at a specific wave length was monitored by a photocell-amplifier system and the absolute intensity of the beam was measured by a thermopile–galvanometer system calibrated against a lamp from the National Bureau of Standards. Details of the procedures are available in the original dissertation.[1]

Procedure.—A calibrated amount of a mixed solution containing about 0.1 mole/l. of diiodoethylene and about 10^{-4} mole/l. of isotopically labelled iodine was added to the sidearm of a cell and was degassed by repeated freezing and evacuation. It was then tipped into the cell and illuminated for an appropriate time with light of known wave length and intensity. After the run, the iodine was extracted with aqueous sulfite and the radioactivity of the resulting solution was measured with a commercial jacketed counter. The extent of exchange could be calculated from the known concentrations and the amount of radioactivity extractable from an unilluminated solution.

Unless otherwise noted, twelve runs were conducted at each wave length for each solvent. As equation 3 indicates, quantum yields were calculated by comparing rates at different wave lengths. In order to make certain that differences in these rates were not confounded with time-dependent changes in lamps, procedure, etc., the experiments with a specific light source followed a random sequence of wave lengths. Although duplicate measurements were generally in reasonable agreement, occasional runs in hexane were very much slower than the others under the same conditions. Since non-absorbing impurities might tend to slow the rate of a photochemical radical chain reaction but are not apt to speed it up, the slow runs were regarded with suspicion. In the hexane experiments reported here, the top third of all rate measurements at a particular wave length were averaged and runs less than 70% of this average rate were rejected. The rest were averaged. All runs in hexachlorobutadiene were included in the averages.

Quoted probable errors in quantum yields are calculated from uncertainties in exchange rates at each wave length assigned as 90% confidence limits by means of a standard t test.

Results

The results of the measurements in hexane and in hexachlorobutadiene-1,3 are presented in Tables I and II. The quantum yields in the last column were computed by equation 3 with the use of quantum yields in the same solvents measured previously.[5]

Similar experiments in hexachlorobutadiene at 4047 Å. indicated so much exchange that the apparent quantum yield was 0.78. This big increase beyond the 0.075 at 4358 Å. is hardly credible. This solvent is also absorbing considerable light at 4047 Å., and we believe the high apparent quantum yield is due to chains initiated by pho-

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[3] D. Booth and R. M. Noyes, THIS JOURNAL, **82**, 1868 (1960).

[4] R. M. Noyes, R. G. Dickinson and V. Schomaker, *ibid.*, **67**, 1319 (1945).

[5] F. W. Lampe and R. M. Noyes, *ibid.*, **76**, 2140 (1954).

[6] H. Rosman and R. M. Noyes, *ibid.*, **80**, 2410 (1958).

TABLE I

QUANTUM YIELD MEASUREMENTS IN HEXANE AT 25°

λ, Å.	$q \times 10^{-10}$, quanta/ml. sec.	b, mole/l.	$R \times 10^8$, mole/l. sec.	$(R^2/b^2q) \times 10^4$, l./mole sec.	ϕ
4047	2.16	0.0893	2.10^{a}	11.6^{h}	0.83 ± 0.18
	2.70	.0893	1.93^{b}		
4358	60.4	.0882	8.44^{c}	9.28^{h}	.66 ± .04^{i}
	56.6	.0882	7.70^{a}		
	56.6	.0988	9.86^{d}		
5461	985	.0988	30.4^{e}	6.38^{h}	.46 ± .07
	1040	.0988	36.0^{e}		
	1000	.0893	28.1^{f}		
5790	99.4	.0988	9.7^{d}	5.03^{h}	.36 ± .13
	91.6	.0893	5.0^{g}		
6430	655	.0994	14.3	1.90	.14 ± .03
7350	403	.0994	10.3	1.60	.11 ± .02

[a] Average of 3 runs. [b] Average of 8 runs. [c] Average of 13 runs. [d] Average of 5 runs. [e] Average of 2 runs. [f] Average of 4 runs. [g] 1 run. [h] A weighted mean was used here. [i] From ref. 5.

TABLE II

QUANTUM YIELD MEASUREMENTS IN HEXACHLOROBUTADIENE-1,3 AT 25°

λ, Å.	$q \times 10^{-10}$, quanta/ml. sec.	b, mole/l.	$R \times 10^8$, mole/l. sec.	$(R^2/b^2q) \times 10^5$, l./mole sec.	ϕ
4358	386	0.1018	5.08	3.89	0.075 ± 0.009^{a}
5461	5320	.1018	13.0	1.85	.036 ± .014
5790	670	.1018	3.30	0.95	.018 ± .006
6430	949	.1018	4.37	1.17	.023 ± .007
7350	518	.1018	3.05	1.05	.020 ± .006

[a] From ref. 5.

tolysis of solvent; these determinations have been discarded.

We were unable to extend the measurements to 3650 Å. in any solvent. The diiodoethylene absorbs at this wave length, and exchange is initiated by the absorption.

The data illustrate a rather disturbing effect that has been noticed before but not adequately explained. The absolute rates of exchange (R) in hexane at 4358 Å. are intermediate between predictions from the data of Zimmerman and Noyes[7] and those of Rosman and Noyes,[6] and the absolute rates in hexachlorobutadiene are less by about a factor of three than predicted by the data of Rosman and Noyes.[6] Even though these absolute rates of exchange show considerable variations in different solvent preparations, lifetimes of iodine atoms in these solvents can be measured reproducibly and have values consistent with independent measurements by other methods in other laboratories. Despite the discrepancies in absolute rates, we are confident that the measurements reported here do indeed determine relative quantum yields.

We do not have similar confidence in some unreported measurements in carbon tetrachloride. Supposedly duplicate experiments showed wide fluctuations in rate of exchange but were invariably very much slower than predicted from the data of Rosman and Noyes.[6] Quantum yields calculated from equation 3 did not show anticipated trends with wave length but seemed more reasonable if it was assumed that chains were terminated by processes that were first order rather than second order in iodine atoms. The solvent apparently contained some impurity that was interfering with the measurements.

Discussion

Theoretical Prediction of Quantum Yields.—If E is the energy to dissociate an iodine molecule into atoms, the atoms produced start to separate in exactly opposite directions with total kinetic energy $h\nu - E$ in excess of normal thermal energies. They will be slowed rapidly by solvent interactions and subsequently may encounter each other and recombine. In another publication,[8] we have developed the equations to treat this situation if the frictional force per unit area on a moving atom is the same as on a macroscopic sphere. The result is

$$1 - \phi = \frac{\beta'}{1 + \dfrac{\sqrt{m(h\nu - E)}}{6\pi\eta a^2}} \qquad (4)$$

where m is the mass of an atom of radius a, η is the viscosity of the solvent and β' is the probability two atoms separating with normal thermal velocities subsequently will recombine.

If the two atoms are sure to combine if they encounter each other, β' can be predicted by the same model with $^3/_2\ kT$ as the initial kinetic energy of separation of the atoms.[3] Then

$$\beta' = \frac{1}{1 + \dfrac{\sqrt{mkT/24}}{\pi\eta a^2}} \qquad (5)$$

These equations permit unequivocal prediction of quantum yields without application of any parameters not capable of independent measurement, but the equations are based on a model that regards the solvent as a continuum exhibiting its macroscopic viscosity at distances smaller than the diameter of a single atom.

Comparison of Theory with Experiment.—We have used equations 4 and 5 to predict quantum yields in these solvents. The application assumed that a = 2.15 Å. and that E = 35.5 kcal./mole. This latter assumption implies that every molecule that absorbs a quantum dissociates into two $^2P_{3/2}$ atoms rather than forming a $^2P_{1/2}$ atom with an additional 22 kcal. of energy. The formation of only $^2P_{3/2}$ atoms would occur if excited molecules always undergo dissociative predissociation induced by the solvent; the efficiency of argon at quenching the fluorescence of gaseous iodine[9] makes it plausible that the solvent would be very efficient at inducing this predissociation.

The calculations with equation 5 gave β' = 0.875 for hexane (0.0029 poise) and 0.986 for

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[7] J. Zimmerman and R. M. Noyes, *J. Chem. Phys.*, **18**, 658 (1950).

[8] R. M. Noyes, *Z. Elektrochem.* (in press).

[9] L. A. Turner, *Z. Physik*, **65**, 464 (1930).

hexachlorobutadiene (0.030 poise). Tables III and IV present the quantum yields calculated for the different wave lengths by inserting these β' values in equation 4. The tables also contain a quantity designated s_t-2a where s_t is the separation of centers of the atoms when they start random diffusion. Then s_t-2a is the distance separating the peripheries of the atoms at this time.

TABLE III

COMPARISON OF THEORY AND EXPERIMENT IN HEXANE (0.0029 POISE)

λ, Å.	$h\nu - E$, kcal./mole	ϕ, obsd.	ϕ, calcd.	$s_t - 2a$, Å.
4047	35.0	0.83	0.54	3.87
4358	30.0	.66	.52	3.58
5461	16.6	.46	.46	2.69
5790	13.9	.36	.44	2.45
6430	8.9	.14	.40	1.96
7350	3.3	.11	.31	1.21

TABLE IV

COMPARISON OF THEORY AND EXPERIMENT IN HEXACHLOROBUTADIENE (0.030 POISE)

λ, Å.	$h\nu - E$, kcal./mole	ϕ, obsd.	ϕ, calcd.	$s_t - 2a$, Å.
4358	30.0	0.075	0.087	0.35
5461	16.6	.036	.070	.26
5790	13.9	.018	.065	.24
6430	8.9	.023	.055	.19
7350	3.3	.020	.040	.12

Conclusions about the Dissociation Process.—Near 4358 Å., the observed and calculated quantum yields are in reasonable agreement. At very long wave lengths, the values of β' predict that the quantum yields will approach limiting values of 0.125 in hexane and 0.014 in hexachlorobutadiene; these predicted limits are remarkably close to the quantum yields observed at the longest wave lengths studied.

Despite these excellent correlations at the limiting wave lengths, theory and experiment diverge badly at intermediate wave lengths. Equation 4 can be shown to predict that $\phi/(1-\phi)$ is a linear function of $\sqrt{h\nu - E}$. This means that for quanta having energy considerably in excess of E the quantum yields should change rather slowly with wave length but ϕ should decrease steeply as the wave length approaches the convergence limit for dissociation of the molecule. The experiments indicate a very different behavior; the quantum yields decrease rapidly with increasing wave length while there is still much more than enough energy to cause dissociation and the quantum yields change very little as the excess energy decreases from 8.9 to 3.3 kcal./mole. The quantity $\phi/(1-\phi)$ is much more nearly linear in $(h\nu - E)^2$ than in the square root as predicted.

These discrepancies undoubtedly arise because it is not permissible to treat the solvent as a viscous continuum at distances of the order of a molecular diameter and the nature of the discrepancies provides direct support for a model originally proposed by Rabinowitch.[10] If two atoms are separated by only a few tenths of an Ångström between their peripheries, the effect of the surrounding solvent molecules is usually to force the atoms toward each other so that they are more apt to come together than would be expected if they diffused completely independently of each other. However, if the atoms are separated sufficiently that two solvent molecules can squeeze between them and almost make contact along the line of centers of the atoms, the most probable distribution of solvent molecules will tend to force the atoms farther apart and will make them less apt to come together than would be expected if they were located in a viscous continuum. The theory developed here uses an averaged interaction and will tend to predict high quantum yields for low energy quanta and to predict low quantum yields for high energy quanta. The predicted and measured quantum yields should be in agreement when s_t-2a approaches but is still less than a molecular diameter. At very high energies where s_t-2a corresponds to a few molecular diameters, the continuum model should again be in fairly satisfactory agreement with experiment, but quantum yields would be very close to unity and comparison would be difficult.

The Rabinowitch model has been invoked frequently to explain "cage" effects of forcing molecules together from very small separations. We believe that these data provide the first experimental support for the other aspect of the model that the solvent can also act preferentially to keep apart species initially at slightly larger separations.

The above emphasis on $s_t - 2a$ is obviously an over-simplification. If an atom in a dissociating molecule is directed exactly between a pair of solvent molecules, it will need very little energy for it to attain a considerable separation from its partner in the original iodine molecule, while "head-on" collisions of both iodine atoms with solvent molecules will lead to recombination even for a rather energetic quantum. Presumably these directional effects become more important as the kinetic energies of separation become less. The apparent existence of a limiting quantum yield at longer wave lengths suggests that escape or recombination of atoms is determined more by chance orientation of solvent molecules than by the exact small amount by which the energy of the quantum exceeds the bond strength. If this interpretation is correct, it is largely fortuitous that the limiting quantum yields agree so well with the values of $1-\beta'$ calculated from the continuum model.

Magnitudes of Diffusive Displacements.—Extrapolation of these quantum yields provides the first experimental measure of β', the probability two atoms separating from each other with thermal energies will undergo recombination. If recombination occurs at every encounter, then equations developed previously[11] permit calculation of the root-mean-square displacement distance for diffusion of iodine atoms in these solvents. Application of the equations gives 0.76 Å. in hexane and 0.13 Å. in hexachlorobutadiene. The results are

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(10) E. Rabinowitch, *Trans. Faraday Soc.*, **33**, 1225 (1937).

(11) R. M. Noyes, THIS JOURNAL, **78**, 5486 (1956).

more consistent with a model for diffusion in which there is no potential barrier to displacement than they are to a model in which diffusion involves an activation energy of a few kcal./mole, and the value in hexachlorobutadiene is probably too small to be plausible even if displacements are opposed by no barriers whatsoever. However, the equations used in this argument tacitly assumed that the solvent could be treated as a continuum. Therefore the argument about energy barriers is suspect.

Summary.—If solvent is regarded as a continuum, rather simple mathematical expressions can be derived. These expressions make predictions without disposable parameters that are often in remarkably good agreement with experimental observation but more detailed comparison reveals systematic discrepancies. Any further progress must introduce the discrete molecular nature of the solvent and it should do so in a manner susceptible to quantitative experimental test.

We do not see any tractable conventional mathematical approach to handle this problem of a discrete particulate solvent but we have hopes that the next refinement of theory can be attained by digital computer techniques already developed by Professor B. J. Alder of the University of California.[12]

Acknowledgments.—The experimental work was carried out at Columbia University and was supported in part by the U. S. Atomic Energy Commission under Contract AT(30-1)-1314. One of us (L.F.M.) was the recipient of a National Science Foundation Science Faculty Fellowship. The development of the theory and preparation of the final paper were carried out at the University of Oregon and were supported in part by the U. S. Atomic Energy Commission under Contract AT(45-1)-1310.

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[12] B. J. Alder and T. Wainwright, "Proceedings of International Symposium on Transport Processes in Statistical Mechanics," Interscience Publishers, Inc., New York, N. Y., 1958, pp. 97–131.

EUGENE, OREGON

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AND SPECTROSCOPY LABORATORY, MASSACHUSETTS INSTITUTE OF TECHNOLOGY]

Vibrational Spectra and Structure of the Tropilidene Molecule[1]

BY M. V. EVANS[2] AND R. C. LORD

RECEIVED JUNE 1, 1959

Study of the Raman spectrum of tropilidene and its infrared spectrum between 300 and 4000 cm.$^{-1}$ shows that the double-bond vibrations of this molecule have surprisingly low frequencies, high intensities in the Raman effect and very weak infrared absorption. Neither of the two structures most often considered for tropilidene—1,3,5-cycloheptatriene and bicyclo-[4.1.0]hepta-2,4-diene—is in complete accord with these and certain other spectroscopic results. An earlier suggestion of the authors that these characteristics indicate a bicyclo[3.2.0]hepta-2,5-diene structure has been disproved by the synthesis and spectroscopic study of this compound. Its spectra and other properties confirm the bicyclic structure but show that it is not tropilidene. The tropilidene structure which best fits the spectroscopic data is a planar quasi-aromatic ring of C_{2v} symmetry, as originally suggested by Doering and Knox, although a structure in which the CH_2 group is displaced slightly out of the molecular plane cannot be excluded. The infrared and Raman data have been interpreted on the C_{2v} basis. The entropy of tropilidene vapor has been calculated to be $S^0_{298} = 76.0$ cal./mole/deg., as compared with the measured value 75.44 ± 0.25. The discrepancy is probably due to uncertainties in the calculation, although the fact that the calculated value is larger suggests that there may be some residual entropy in crystalline tropilidene at low temperature. Infrared and Raman spectra are also reported for 3,7,7-trimethyltropilidene and 3,4,7,7-tetramethyltropilidene.

Introduction

The discovery of the aromatic nature of the tropylium ion ($C_7H_7^+$) and the growing interest in the related substances tropone, heptafulvene, tropolone and azulene[3] have created new interest in the structure of their parent hydrocarbon tropilidene. Tropilidene was first prepared from the alkaloid tropine by Ladenburg[4] in 1881 and an investigation of the structure of the hydrocarbon was carried out by Willstätter[4] in 1901. Willstätter repeated Ladenburg's synthesis and then prepared tropilidene by several other routes starting from cycloheptene. This set of synthetic methods convinced him that tropilidene had the structure 1,3,5-cycloheptatriene (I), but he also considered the structures bicyclo[4.1.0]hepta-4,6-diene (II), bicyclo-[3.2.0]hepta-2,5-diene (III) and bicyclo[2.21]hepta-2,5-diene (IV) as shown in Fig. 1. Willstätter ruled out structure IV because a hydrocarbon of that structure was known and had different physical and chemical properties. Structure III was rejected by him because he felt that there was no reason to suppose that this type of structure would absorb three moles of hydrogen to give cycloheptane, as was observed for tropilidene and, further, it was difficult for him to explain why such a structure should be formed in any of the reactions leading to tropilidene. Structure II was more acceptable in that an analogous ring system was supposed to be formed in the case of the Buchner acids,[5] but the bicyclo ring system was supposed to be very labile and susceptible to rearrangement to the cycloheptatriene ring-system. This, plus the fact

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[1] This paper is based on the Ph.D. thesis of M. V. Evans submitted to the Massachusetts Institute of Technology in January, 1958. The work described was supported in part by the National Science Foundation (Grant G-1892).

[2] Department of Chemistry, University of Wisconsin, Madison, Wisconsin.

[3] (a) A. W. Johnson, *J. Chem. Soc.*, 1331 (1954); (b) T. Nozoe, *Kagaku* (*Science*), **21**, 564 (1951).

[4] (a) A. Ladenburg, *Ber.*, **14**, 2129 (1881); (b) R. Willstätter, *Liebig's Ann.*, **317**, 204 (1901).

[5] E. Buchner, *Ber.*, **31**, 2241 (1898).