# **844.** *The Decomposition of Arylazotriarylmethanes.*

By G. L. Davies, D. H. Hey, and Gareth H. Williams.

The energies and entropies of activation have been measured for the decomposition of phenylazotriphenylmethane in a number of solvents, and of a number of substituted arylazotriarylmethanes in toluene solution. Although only small differences in the rates of decomposition are shown, the activation parameters are found to exhibit much more pronounced variations, which tend to compensate one another. The mechanism of the decomposition of these and allied compounds is discussed, and explanations are suggested for the effects of solvents and substituents on the activation parameters based on a combination of the influence of resonance and solvation phenomena.

PHENYLAZOTRIPHENYLMETHANE * was first prepared by Gomberg [1] by reaction of phenylhydrazine with bromotriphenylmethane, followed by oxidation of the resulting hydrazo-compound with pentyl nitrite. It was found to decompose at its melting point (111°) with evolution of nitrogen, yielding a residue from which tetraphenylmethane could be isolated in very small yield. α-Naphthylazotriphenylmethane and some other arylazotriphenylmethanes were prepared by Gomberg and Campbell,[2] but attempts to determine the products of decomposition were unsuccessful. Wieland, Popper, and Seefried [3] allowed phenylazotriphenylmethane to decompose at 80° in ligroin in an atmosphere of nitrogen and found that triphenylmethyl radicals could be identified spectroscopically in the resulting solution. After removal of these as triphenylmethyl peroxide by passing oxygen through the solution, small amounts of triphenylmethane and tetraphenylmethane were obtained. Apart from the small amount accounted for by the formation of tetraphenylmethane, the fate of the phenyl radicals, which were assumed to be formed, remained unknown. Further experiments showed that benzene was formed, but no trace of the expected diphenyl was found. This is understandable in view of the now well-established conclusion that when phenyl radicals are formed in dilute solution the amount of dimerisation which takes place is very small. Hey [4] allowed phenylazotriphenylmethane to decompose in solution in benzene, chlorobenzene, and nitrobenzene, and showed that in benzene solution diphenyl was formed. From the decomposition in chlorobenzene, 4-chlorodiphenyl was obtained, but triphenylmethane was the only product isolated from the decomposition in nitrobenzene. In the present investigation, however, the reaction in nitrobenzene has been re-examined, and 4-nitrodiphenyl has been shown to be one of the products. The formation of these unsymmetrically substituted diaryl products was regarded as an indication that phenyl radicals were formed in the decomposition of phenylazotriphenylmethane. These conclusions were confirmed and extended by Wieland and

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* The well-understood name, phenylazotriphenylmethane (and in general, arylazotriarylmethane), is used in this communication for the compound $PhN{:}N{\cdot}CPh_3$ pending clarification of the rules governing the nomenclature of this class of compound.

[1] Gomberg, *Ber.*, 1897, **30**, 2043.

[2] Gomberg and Campbell, *J. Amer. Chem. Soc.*, 1898, **20**, 773.

[3] Wieland, Popper, and Seefried, *Ber.*, 1922, **55**, 1816.

[4] Hey, *J.*, 1934, 1966.

his co-workers,[5] who obtained 2- and 4-methyldiphenyl from the decomposition of phenylazotriphenylmethane in toluene, and 2- and 4-phenylpyridine from its decomposition in pyridine. These workers therefore put forward the following scheme for the decomposition in aromatic solvents :

$$\mathrm{Ph{\cdot}N{:}N{\cdot}CPh_3} \longrightarrow \mathrm{Ph{\cdot}} + \mathrm{N_2} + \mathrm{{\cdot}CPh_3} \quad (1)$$

$$\mathrm{Ph{\cdot}} + \mathrm{ArH} \longrightarrow \mathrm{PhAr} + \mathrm{H{\cdot}} \quad (2)$$

$$\mathrm{H{\cdot}} + \mathrm{{\cdot}CPh_3} \longrightarrow \mathrm{Ph_3CH} \quad (3)$$

More recent work [(Mrs.) Adams, Hey, Mamalis, and Parker [6]] has shown that 3-phenylpyridine is also formed in the reaction of phenylazotriphenylmethane with pyridine. Attention was drawn by Hey and Waters [7] to the analogy between these reactions and those of nitrosoacetanilide and of sodium benzenediazoate with the same solvents. All these reactions were considered to involve phenyl radicals as intermediates.

Further evidence for the existence of free radicals in the reactions of arylazotriarylmethanes was obtained by Hey and Misra,[8] who showed that these compounds were capable of initiating the polymerisation of styrene and methyl methacrylate, and that both aryl and triarylmethyl radicals were incorporated in the polymers. Hey, Stirling, and and Williams [9] have further confirmed this conclusion by analysis of the isomeric products of the reaction of phenylazotriphenylmethane with pyridine, and comparison of the result with those for the phenylation of pyridine under the same conditions with benzoyl peroxide, lead tetrabenzoate, phenyl iodosobenzoate, and nitrosoacetanilide.

After the inception of the work described in this communication, the kinetic aspects of the decomposition of arylazotriarylmethanes attracted the interest of several groups of workers. Huisgen and Nakaten [10] confirmed that the mechanism originally put forward by Wieland and his co-workers [5] is correct. These workers showed kinetically that no chain mechanism can be operative, and concluded from the nature of the products of the decomposition in various solvents, and in the presence of iodine, that the mechanism is not of the " kryptoradical " type similar to that advanced by Huisgen and Horeld [11] for the decomposition of aromatic diazo-acylates. Huisgen and Nakaten [10] also demonstrated the presence of hydrogen atoms in the reaction mixture by the use of the reduction indicator triphenyltetrazolium chloride. In this connection it was also observed that a small amount of aniline was formed in the decomposition in nitrobenzene. This last result has been confirmed in the present work.

The results of Cohen and Wang,[12] Alder and Leffler,[13] Leffler and Hubbard,[14] and Cohen, Leffler, and Barbato [15] will be discussed together with the results obtained in the present work in a later Section of this paper.

If Wieland's mechanism [5] involving primary dissociation into phenyl and triarylmethyl radicals and nitrogen be accepted, it is obvious that the rate of decomposition must be dependent upon the stability of the radicals produced by the primary dissociation, insofar as the stability of the transition state and hence the activation energy for the dissociation, are influenced or paralleled by this factor. Indeed, it was on the basis of this effect alone that Cohen and Wang [12] attempted to explain the variation in activation energy occasioned by the introduction of various substituents X in compounds of the type $p\text{-X}{\cdot}\mathrm{C_6H_4{\cdot}N{:}N{\cdot}CPh_3}$. In order to establish the reality of such a concept, it is of interest to consider the stability of phenylazotriphenylmethane in relation to some other azo-compounds. These compounds are listed in Table 1 (cf. Wieland, vom Hove, and Börner [16]),

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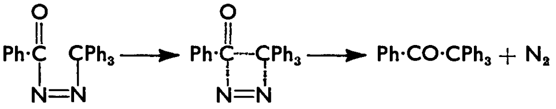
[5] Wieland, Heyman, Tsatsas, Juchum, Varvoglis, Labriola, Dobbelstein, and Boyd-Barrett, *Annalen*, 1934, **514**, 145.
[6] (Mrs.) Adams, Hey, Mamalis, and Parker, *J.*, 1949, 3181.
[7] Hey and Waters, *Chem. Rev.*, 1937, **21**, 184.
[8] Hey and Misra, *J.*, 1949, 1807.
[9] Hey, Stirling, and Williams, *J.*, 1955, 3963.
[10] Huisgen and Nakaten, *Annalen*, 1954, **586**, 70.
[11] Huisgen and Horeld, *ibid.*, 1949, **562**, 137.
[12] Cohen and Wang, *J. Amer. Chem. Soc.*, 1953, **75**, 5504.
[13] Alder and Leffler, *ibid.*, 1954, **76**, 1425.
[14] Leffler and Hubbard, *J. Org. Chem.*, 1954, **19**, 1089.
[15] Cohen, Leffler, and Barbato, *J. Amer. Chem. Soc.*, 1954, **76**, 4169.
[16] Wieland, vom Hove, and Börner, *Annalen*, 1926, **446**, 31.

in order of increasing stability. The decomposition of benzoylazotriphenylmethane was studied by Wieland, vom Hove, and Börner,[16] and that of other acylazotriphenylmethanes by Wieland, Hintermaier, and Dennstedt,[18] and Wieland and his co-workers.[5] It was shown that benzoylazotriphenylmethane decomposes in xylene solution much more readily than phenylazotriphenylmethane: nitrogen is evolved, and benzoyltriphenylmethane is obtained in up to 70% yield. It was suggested that in contrast to phenylazotriphenylmethane, where only about 5% of tetraphenylmethane is formed, and which was therefore considered to proceed by the mechanism involving phenyl and triphenylmethyl radicals, benzoylazotriphenylmethane decomposed by an intramolecular mechanism (4), which does not involve free-radical intermediates. In support of this scheme, the stability of azodibenzoyl was cited as evidence of the relative strength of the Ph·CO–N bond when compared with that of the $Ph_3C$–N bond. A re-interpretation of these results is, however, now possible in the light of more modern ideas concerning the relative stability of radicals. The benzoyl radical, by virtue of the contribution of canonical forms such as (I) and (II) to the resonance hybrid, would be expected to be a more stable, and consequently less reactive radical, than phenyl.

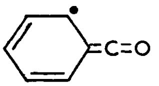
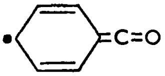
TABLE 1.

| Compound | Stability | Compound | Stability |
|---|---|---|---|
| Azotriphenylmethane<br>$Ph_3C{\cdot}N{:}N{\cdot}CPh_3$ | Does not exist | Azodibenzoyl *<br>$Ph{\cdot}CO{\cdot}N{:}N{\cdot}COPh$ | Incomplete decomp. at 135° |
| Benzylazotriphenylmethane<br>$Ph_3C{\cdot}N{:}N{\cdot}CH_2Ph$ | Does not exist | Benzoylazobenzene<br>$Ph{\cdot}CO{\cdot}N{:}NPh$ | Stable at 135° |
| Benzoylazotriphenylmethane<br>$Ph_3C{\cdot}N{:}N{\cdot}COPh$ | Decomp. at room temp. | Azobenzene<br>$Ph{\cdot}N{:}NPh$ | Very stable (b. p. 293° without decomp.) |
| Phenylazotriphenylmethane<br>$Ph_3C{\cdot}N{:}NPh$ | Decomp. at 70—80° | | |

* Leffler and Bond,[17] recently showed that azodibenzoyl decomposes slowly at 110° in benzene solution to give a complex mixture.



. . . . . (4)

(I)   (II)

This decrease in reactivity might well reduce considerably, or even eliminate, the ability of benzoyl radicals to react with an aromatic solvent. In such circumstances the life of a benzoyl radical in solution must be sufficiently prolonged to allow fruitful collisions with triphenylmethyl radicals, yielding benzoyltriphenylmethane. Thus the production of benzoyltriphenylmethane, and the relative stability of benzoylazotriphenylmethane when compared with phenylazotriphenylmethane, are not inconsistent with a mechanism involving primary dissociation into free radicals, in view of the expected non-reactivity of the benzoyl radical. This interpretation is supported by the observation of Wieland, Hintermaier, and Dennstedt [18] that benzylazotriphenylmethane is unstable, all attempts to prepare it leading to *asym.*-tetraphenylethane. This would be expected from the above considerations, in view of the resonance-stabilisation of the benzyl radical, whose low reactivity is well known. It has also been shown by Wieland, Ploetz, and Indest [19] that in the decomposition of benzoylazotriphenylmethane, the yield of nitrogen is not quantitative, and that a small amount of benzoylhydrazine is formed. This cannot be accommodated on the basis of an intramolecular mechanism, but is consistent with the postulate of a primary dissociation into free radicals, provided that it is assumed that the

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[17] Leffler and Bond, *J. Amer. Chem. Soc.*, 1956, **78**, 335.
[18] Wieland, Hintermaier, and Dennstedt, *Annalen*, 1927, **452**, 1.
[19] Wieland, Ploetz, and Indest, *ibid.*, 1937, **532**, 166.

two bonds are not broken simultaneously, but that the initial stage is the production of triphenylmethyl and benzoylazo-radicals, some of which subsequently lose nitrogen (5 and 6) :

$$\text{Ph·CO·N:N·CPh}_3 \longrightarrow \text{Ph·CO·N:N·} + \text{·CPh}_3 \quad . \; . \; . \; . \; . \; . \; . \quad (5)$$

$$\text{Ph·CO·N:N·} \longrightarrow \text{Ph·CO·} + \text{N}_2 \quad . \; . \; . \; . \; . \; . \; . \; . \; . \quad (6)$$

Thus it appears that Wieland's mechanism involving primary dissociation is consistent with the known facts concerning the decomposition of azo-compounds of this type. The present investigation was carried out with the object of confirming this postulate as applied to arylazotriarylmethanes and of discovering what other factors, if any, contribute to the stability of compounds of this type.

## EXPERIMENTAL

*Materials.*—Arylazotriarylmethanes were prepared by the general method employed by Gomberg and Campbell,[2] Gomberg and Berger,[20] and Wieland, Popper, and Seefried,[3] in which an arylhydrazine (2 mols.) is treated with the appropriate triarylchloromethane (1 mol.) in ether. Oxidation of the resulting arylhydrazotriarylmethane was carried out by the method of Wieland, vom Hove, and Börner,[16] using alkaline potassium ferricyanide, except that for *m*- and *p*-nitrophenylazotriphenylmethane pentyl nitrite was used (Gomberg and Campbell [2]).

Phenylazotriphenylmethane crystallised from benzene–ethanol in yellow needles, m. p. 111° (decomp.). *p*-Tolylazotriphenylmethane, m. p. 103·5° (decomp.) (15·9 g.), was obtained from triphenylchloromethane (27·8 g.) and *p*-tolylhydrazine (24·4 g.), which was prepared from *p*-toluidine by Macpherson and Stratton's method [21] (Gomberg and Campbell [2] reported m. p. 103·5° for this compound). *p*-Chlorophenylazotriphenylmethane, m. p. 108° (decomp.), and *p*-bromophenylazotriphenylmethane, m. p. 112° (decomp.), were prepared as described by Hey and Misra.[8]

*p*-Nitrophenylazotriphenylmethane was prepared by a modification of Gomberg and Campbell's method.[2] A saturated solution of triphenylchloromethane (9·0 g.) in ethyl acetate was added to a boiling solution of *p*-nitrophenylhydrazine (10·2 g.) in ethyl acetate (150 ml.). The mixture was boiled under reflux for 20 min., during which the brownish-yellow *p*-nitrophenylhydrazine hydrochloride was precipitated. After cooling, the mixture was filtered and most of the ethyl acetate distilled off. Ethanol was added to the residue after cooling, to precipitate the *p*-nitrophenylhydrazotriphenylmethane (10 g.; m. p. 170°). This product (10 g.) was suspended in ether (250 ml.) and an excess of pentyl nitrite was added together with a drop of acetyl chloride to start the reaction. The suspension was boiled under reflux for 5—10 min. The ether was allowed to evaporate at room temperature, orange crystals of *p*-nitrophenylazotriphenylmethane being deposited. The product had m. p. 120° (decomp.) (9·29 g.) after purification by precipitation from benzene by ethanol. Gomberg and Campbell [2] reported m. p. 118·5° (decomp.).

*m*-Tolylhydrazine was prepared by the method used by Macpherson and Stratton [21] for *p*-tolylhydrazine. The quantities of reagents and experimental details are identical with those described for the latter compound, except that, on neutralisation of the hydrochloride, *m*-tolylhydrazine separated as an oil. This was extracted with ether, and the crude product obtained from the dried extract after removal of the ether was distilled under vacuum, yielding *m*-tolylhydrazine (b. p. 132—134°/16 mm.; 243°/760 mm.), in 76·5% yield. Buckha and Schachtabeck [22] reported b. p. 240—244° for this compound. *m*-Tolylhydrazine (12·2 g.) was allowed to react in ethereal solution with triphenylchloromethane (13·9 g.), by use of the procedure already described except that in this case heating was maintained for 5 hr. The resulting hydrazo-compound was oxidised with potassium ferricyanide (80 g.) in water (300 ml.) and 2N-sodium hydroxide (100 ml.). After being ground with a little ethanol and collected, the product was dissolved in the minimum quantity of benzene, and precipitated by the addition of an equal volume of ethanol. This procedure was repeated four times, to give m-*tolylazotriphenylmethane* (10·5 g.), m. p. 101·5° (decomp.) (Found: C, 85·8; H, 6·3. $C_{26}H_{22}N_2$ requires C, 86·2; H, 6·1%).

*m*-Chlorophenylazotriphenylmethane, m. p. 107° (decomp.) (11·0 g.), was prepared from

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[20] Gomberg and Berger, *Ber.*, 1903, **36**, 1088.

[21] Macpherson and Stratton, *J. Amer. Chem. Soc.*, 1915, **37**, 908.

[22] Buckha and Schachtabeck, *Ber.*, 1889, **22**, 841.

*m*-chlorophenylhydrazine (b. p. 160—164°/21 mm.; 14·25 g.) and triphenylchloromethane (13·9 g.); Gomberg and Campbell[2] reported m. p. 109°. *m*-Nitrophenylazotriphenylmethane, m. p. 111° (decomp.) (14 g.), was prepared from *m*-nitrophenylhydrazine (m. p. 93°; 15·3 g.), obtained in 52% yield by Bischler and Brodsky's method,[23] and triphenylchloromethane (13·9 g.) by the method used for the preparation of the *para*-isomeride; Gomberg and Campbell[2] reported m. p. 111—112° (decomp.).

Tri-*p*-tolylmethanol was prepared by Mothwurf's procedure,[24] but from methyl *p*-toluate (20 g.) and *p*-bromotoluene (51·3 g.). The product was subjected to steam-distillation to remove volatile impurities and to the residual thick oil dissolved in a small amount of benzene was added light petroleum (b. p. 60—80°). This solution was passed through a short alumina column, which was eluted with light petroleum (b. p. 60—80°). The combined eluate was evaporated to small bulk and allowed to cool; tri-*p*-tolylmethanol crystallised in white plates, m. p. 97° (14 g.). Mothwurf[24] reported m. p. 96·5°. This alcohol (14 g.) was boiled with acetyl chloride (100 ml.) for 15 min. After removal of the excess of acetyl chloride by distillation the residual chlorotri-*p*-tolylmethane was recrystallised from light petroleum (yield, 12·5 g.; m. p. 180°); Mothwurf[24] reported m. p. 181°. Phenylazotri-*p*-tolylmethane, m. p. 113° (decomp.) (7·3 g.), was prepared by the general method described, from phenylhydrazine (6·5 g.) and chlorotri-*p*-tolylmethane (9·6 g.); Mothwurf[24] reported m. p. 113—116° (decomp.).

Tri-*p*-chlorophenylmethanol was prepared by Baeyer's method[25] from *p*-chloroiodobenzene (47·6 g.) (prepared by the iodination of chlorobenzene by Datta and Chatterjee's method[26]), magnesium (4·9 g.), and methyl *p*-chlorobenzoate (15 g.). Purification of the product by the method described for tri-*p*-tolylmethanol gave tri-*p*-chlorophenylmethanol (11 g.) in colourless hexagonal plates, m. p. 97°: Baeyer[25] reported m. p. 98—98°. Chlorotri-*p*-chlorophenylmethane, m. p. 112—113°, was prepared in 80% yield from tri-*p*-chlorophenylmethanol by the method described for chlorotri-*p*-tolylmethane; Baeyer[25] reported m. p. 113°. *Phenylazotri-*p*-chlorophenylmethane*, m. p. 110° (decomp.) (5·2 g.), was prepared by the general method described above, from phenylhydrazine (4·3 g.) and chlorotri-*p*-chlorophenylmethane (7·6 g.) (Found: C, 66·5; H, 4·1. $C_{25}H_{17}N_2Cl_3$ requires C, 66·4; H, 3·9%).

Tri-*p*-bromophenylmethanol, m. p. 131°, was prepared in 29% yield by the method described for the preparation of tri-*p*-chlorophenylmethanol; Gomberg and Cone[27] reported m. p. 131°. Tri-*p*-bromophenylchloromethane, m. p. 152°, was obtained in 93% yield from tri-*p*-bromophenylmethanol and acetyl chloride in the manner described for the preparation of chlorotri-*p*-chlorophenylmethane; Gomberg and Cone[27] reported 153°.

Phenylazotri-*p*-bromophenylmethane could not be prepared. Tri-*p*-bromophenylchloromethane was condensed with phenylhydrazine by the general method already described. On oxidation of the resulting ethereal solution of *N*-tri-*p*-bromophenylmethyl-*N'*-phenylhydrazine with alkaline potassium ferricyanide, considerable frothing was observed, and a brown tar was obtained from which no azo-compound could be isolated. To a portion of this tar (3 g.) a small amount of ethanol was added. Scratching with a glass rod caused the tar to solidify, and after it had been allowed to stand for ½ hr. the solid was filtered off, dissolved in benzene, and passed through an alumina column, which was subsequently eluted with 1 : 1 benzene–light petroleum (b. p. 60—80°; 300 ml.). Evaporation of the eluate yielded ethyl tri-*p*-bromophenylmethyl ether (1·3 g.), which was obtained in clusters of colourless prisms, m. p. 206°, alone or mixed with a specimen prepared by Gomberg and Cone's method.[27] Further elution of the column with ethanol (100 ml.) yielded an unidentified substance (0·25 g.), m. p. 172° (Found: C, 46·9; H, 1·9%).

Tri-*p*-nitrophenylmethane[28] (20 g.) was oxidised with chromium trioxide in glacial acetic acid by Fischer and Fischer's method.[29] Recrystallisation of the product from benzene gave tri-*p*-nitrophenylmethanol (9·6 g.), m. p. 191°; Fischer and Fischer[29] reported m. p. 172°, and Montagne[28] reported m. p. 193°. Chlorotri-*p*-nitrophenylmethane was prepared from tri-*p*-nitrophenylmethanol (4·1 g.) by Gomberg's method.[30] Purification of the product by chromatography on alumina, and recrystallisation from benzene, yielded pale orange crystals of *chlorotri-*p*-nitrophenylmethane* (3 g.), m. p. 209° (Found: C, 55·0; H, 2·9. $C_{19}H_{12}O_6N_3Cl$

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[23] Bischler and Brodsky, *Ber.*, 1889, **22**, 2809.
[24] Mothwurf, *Ber.*, 1904, **37**, 3153.
[25] Baeyer, *Ber.*, 1905, **38**, 586.
[26] Datta and Chatterjee, *J. Amer. Chem. Soc.*, 1919, **41**, 293.
[27] Gomberg and Cone, *Ber.*, 1906, **39**, 3284.
[28] Montagne, *Rec. Trav. chim.*, 1905, **24**, 125.
[29] Fischer and Fischer, *Annalen*, 1878, **194**, 256.
[30] Gomberg, *Ber.*, 1904, **37**, 1640.

requires C, 55·1; H, 2·9%). Gomberg[30] failed to purify this compound, and did not record its m. p.

Phenylazotri-*p*-nitrophenylmethane could not be obtained. Phenylhydrazine (1·7 g.) and chlorotri-*p*-nitrophenylmethane (3·6 g.) were boiled under reflux in ether for 24 hr. Oxidation of the resulting solution, after filtration, with alkaline potassium ferricyanide gave only a red tar.

*Purification of Solvents.*—Toluene was boiled under reflux with 1% sodium amalgam for 8 hr. and after filtration was distilled through a 4-ft. helix-packed column. Nitromethane was boiled under reflux in a stream of air for 5 hr. to remove volatile impurities: it was then boiled under reflux for 4 hr. with charcoal, filtered, and fractionally distilled. Acetic acid was boiled for 10 hr. with chromium trioxide and fractionally distilled, the fraction boiling at 118° being collected: it was then fractionally frozen to constant m. p. 16·3°. Nitrobenzene was fractionally frozen several times, dried ($P_2O_5$), and fractionally distilled (b. p. 109°/26 mm.). *n*-Propyl alcohol was shaken with solid sodium hydroxide, filtered, and distilled: after being dried (CaO), it was fractionally distilled.

*Kinetic Measurements.*—The apparatus was so designed that, after the introduction of the azo-compound and the solvent into the reaction vessel, the apparatus could be swept free of air with nitrogen, and the reaction started without opening any part of it to the atmosphere. The reaction flasks were of approx. 30 ml. capacity. Each flask carried a side-arm which could be closed by a tap and was used for the introduction of nitrogen. The upper section of each reaction vessel, which was attached to the lower by means of a B24 joint, carried a stirrer, and a side-arm, which was connected to a nitrometer. The stirrers rotated in tightly fitting polyvinyl chloride glands, which were lubricated with a mixture of Vaseline and liquid paraffin. These glands were found to be completely airtight for pressure differences up to 30 cm. of water—a value which was about 6 times the maximum encountered during a run. The nitrometers were of 50 ml. capacity and could be read to the nearest 0·05 ml. The closed limb of each was fitted with a three-way tap, by means of which the reaction vessel could be connected either to the atmosphere or to the nitrometer. The nitrometers contained water saturated with nitrogen. The reaction flasks were immersed in an oil-filled thermostat, which was accurate to ±0·05°.

Kinetic experiments were conducted as follows. All solvents were saturated with dry nitrogen immediately before use. A weighed portion of the azo-compound was introduced into the reaction vessel in a sealed, thin-walled glass ampoule, which was allowed to float on the solvent. The apparatus was then assembled and the reaction vessel connected to the atmosphere by means of the three-way tap, the closed limb of the nitrometer being full of water. The stirrer was raised above the surface of the solvent and nitrogen was passed through the apparatus for 1 hr. At the end of this time the apparatus was closed to the nitrogen supply, and connected to the nitrometer by the three-way tap. The reaction vessel was lowered into the thermostat and allowed to attain thermal equilibrium. The initial nitrometer reading was taken, and the reaction started by depressing the stirrer to break the glass ampoule. This movement of the stirrer created an error in the initial nitrometer reading, and a correction for this was applied at the end of the run by returning the stirrer to its original position and noting the difference in volume as registered on the nitrometer. This difference was then added to the observed initial reading. Rapid stirring was maintained throughout the reaction. Nitrometer readings were taken at regular intervals, depending on the rate of the particular reaction being observed. The " infinity " reading was taken after an interval of time equal to at least 10 times the half-life of the reaction. A further reading was taken after a few hours to ensure that no change due to leakage or any other cause had taken place. The atmospheric pressure and temperature were found normally to remain sufficiently constant during a run, but were often found to have changed when the time came to take the " infinity " reading. It was usually possible, by means of heaters or fans, to bring the room temperature back to its original value, although a few runs had to be repeated when the difference was too great. The pressure correction was made by raising or lowering the open limb of the nitrometer by the requisite amount. Since all the reactions studied were kinetically of the first order, it was unnecessary to correct individual readings to S.T.P. Velocity constants were calculated from the observed readings according to the first-order law, which, in all cases, was strictly obeyed. All measurements were carried out in duplicate or triplicate.

*Kinetic Results.*—In order to establish the first-order law for the reaction, phenylazotriphenylmethane was allowed to decompose in toluene solution at various concentrations. The results, which are given in Table 2, show that the measured first-order velocity constant $k_1$ is independent of the initial concentration. This result is in accord with the findings by Cohen and

Wang,[12] and is indicative of a unimolecular reaction. All subsequent decompositions were carried out at concentrations within the range shown in Table 2, except that of phenylazotriphenylmethane in *n*-propyl alcohol, where the low solubility demanded a lower concentration (~0·014M).

First-order velocity constants for the decomposition at various temperatures of phenylazotriphenylmethane in various solvents, of *para*- and *meta*-substituted arylazotriphenylmethanes in toluene, and of various phenylazotriarylmethanes in toluene are given in Tables 3—6.

TABLE 2. *Decomposition of phenylazotriphenylmethane in toluene at* 60·35°.

| Initial concn. (M) | $10^4k_1$ (sec.$^{-1}$) | $10^4k_1$ (mean) (sec.$^{-1}$) |
|---|---|---|
| 0·035 | 6·33, 6·29 | 6·31 |
| 0·055 | 6·33, 6·38 | 6·35 |
| 0·075 | 6·33, 6·33 | 6·33 |

TABLE 3. *Decomposition of phenylazotriphenylmethane in various solvents.*

| Solvent | Temp. | $10^4k_1$ (mean) (sec.$^{-1}$) | Solvent | Temp. | $10^4k_1$ (mean) (sec.$^{-1}$) |
|---|---|---|---|---|---|
| Toluene ............... | 49·55° | 1·61 | Acetic acid ......... | 54·65° | 2·90 |
| | 54·65 | 3·00 | | 60·35 | 5·57 |
| | 60·35 | 6·33 | | 65·15 | 10·2 |
| | 65·15 | 11·2 | | | |
| Nitromethane ...... | 54·65 | 2·40 | *n*-Propyl alcohol ... | 54·65 | 2·53 |
| | 60·35 | 5·18 | | 60·35 | 6·00 |
| | 65·15 | 9·36 | | 65·15 | 11·2 |
| Nitrobenzene ......... | 54·65 | 2·37 | | | |
| | 60·35 | 4·80 | | | |
| | 65·15 | 8·49 | | | |

TABLE 4. *Decomposition of* $p$-X·$C_6H_4$·N:N·$CPh_3$ *in toluene.*

| X | Temp. | $10^4k_1$ (mean) (sec.$^{-1}$) | X | Temp. | $10^4k_1$ (mean) (sec.$^{-1}$) |
|---|---|---|---|---|---|
| Me ............... | 49·55° | 1·75 | Br ............... | 54·65° | 1·30 |
| | 54·65 | 3·14 | | 60·35 | 2·63 |
| | 60·35 | 5·98 | | 65·15 | 4·99 |
| | 65·15 | 11·3 | | 70·30 | 8·98 |
| Cl ............... | 54·65 | 1·41 | $NO_2$ ............ | 60·35 | 1·40 |
| | 60·35 | 3·09 | | 65·15 | 2·61 |
| | 65·15 | 5·50 | | 70·30 | 4·87 |
| | 70·30 | 9·67 | | 74·85 | 8·75 |

TABLE 5. *Decomposition of* $m$-X·$C_6H_4$·N:N·$CPh_3$ *in toluene.*

| X | Temp. | $10^4k_1$ (mean) (sec.$^{-1}$) | X | Temp. | $10^4k_1$ (mean) (sec.$^{-1}$) | X | Temp. | $10^4k_1$ (mean)(sec.$^{-1}$ |
|---|---|---|---|---|---|---|---|---|
| Me | 49·55° | 1·55 | Cl | 54·65° | 1·27 | $NO_2$ | 60·35° | 1·35 |
| | 54·65 | 3·22 | | 60·35 | 2·68 | | 65·15 | 2·62 |
| | 60·35 | 6·81 | | 65·15 | 5·45 | | 70·30 | 5·22 |
| | 65·15 | 12·8 | | 70·30 | 10·3 | | 74·85 | 9·25 |

TABLE 6. *Decomposition of* Ph·N:N·C($C_6H_4$X-$p$)$_3$ *in toluene.*

| X | Me | | | | Cl | | | |
|---|---|---|---|---|---|---|---|---|
| Temp. | 44·75° | 49·55° | 54·65° | 60·35° | 44·75° | 49·55° | 54·65° | 60·35° |
| $10^4k_1$ (mean) (sec.$^{-1}$) | 0·776 | 1·62 | 2·98 | 6·21 | 2·34 | 4·80 | 8·72 | 16·7 |

The compounds with X = Br or $NO_2$ decompose under conditions of preparation.

*Decomposition of Phenylazotriphenylmethane in Toluene in the Presence of Iodine.*—This experiment was carried out in order to ascertain whether the rate of decomposition was affected by the nature of the subsequent reactions of the free radicals. Owing to the reversibility of the reaction of triphenylmethane with iodine (cf. Waters [31]), the reaction was carried out in the presence of ethanol and pyridine according to the method used by Ziegler, Ewald, and Orth [32] for the measurement of the rate of decomposition of hexaphenylethane. The ethanol and

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[31] Waters, " The Chemistry of Free Radicals," Oxford Univ. Press, 1950, p. 44.

[32] Ziegler, Ewald, and Orth, *Annalen*, 1930, **479**, 277.

pyridine serve to repress the reverse reaction by reacting with iodotriphenylmethane to form the stable, colourless products, ethyl triphenylmethyl ether and pyridine hydriodide (7 and 8):

$$\mathrm{Ph_3CI + HOEt \longrightarrow Ph_3C{\cdot}OEt + HI} \qquad (7)$$

$$\mathrm{HI + C_5H_5N \longrightarrow C_5H_5N,HI} \qquad (8)$$

A mixture of iodine (1·46 g.), ethanol (2 ml.) and pyridine (4 ml.) was made up to 100 ml. with toluene. A portion (25 ml.) of this solution was transferred to a reaction flask, and the rate of decomposition of phenylazotriphenylmethane determined in the usual way at 60·35°. At the end of the reaction, the solution was titrated against standard sodium thiosulphate. A further portion (25 ml.) of the original solution was similarly titrated, the difference in the two titrations being a measure of the amount of iodine consumed in reaction with the free radicals. The velocity constant for the decomposition was found to be unaltered by the presence of the added substances, and the amount of iodine taken up in the reaction was equal to 90% of that required for reaction with all the phenyl and triphenylmethyl radicals produced. This result confirms unequivocally the conclusion that the fate of the radicals produced is not kinetically significant and that, therefore, the production of the radicals is the rate-determining stage. A similar conclusion has been reached by Huisgen and Nakaten.[10]

*Decomposition of Phenylazotriphenylmethane in Nitrobenzene.*—Acid-extraction of the crude product of the reaction of phenylazotriphenylmethane (10 g.) with nitrobenzene (350 ml.) at 80° revealed the presence of aniline (0·1 g.). The acid-washed product was chromatographed on alumina, and the following products were obtained, which were identified by mixed m. p.: triphenylmethane (1·98 g.), m. p. 92°; triphenylmethanol (0·51 g.), m. p. 162°; 4-nitrodiphenyl (0·64 g.), m. p. 114°. A similar reaction, carried out with the passage of a current of dry oxygen, gave no triphenylmethane but triphenylmethyl peroxide (0·46 g.), m. p. 185°, triphenylmethanol (2·50 g.), m. p. 162°, and 4-nitrodiphenyl (0·46 g.), m. p. 114°.

## DISCUSSION

*Activation Parameters.*—Values of the energy of activation, $E$, the non-exponential factor $B$, and the entropy of activation $\Delta S^*$, for the various reactions studied are given in Tables 7—10. In general, when the same quantity has been measured by previous workers,[12, 14] the agreement between the results is good.

TABLE 7. *Decomposition of phenylazotriphenylmethane in various solvents.*

| Solvent | $E$ (kcal. mole$^{-1}$) | $B$ | $\Delta S^*$ (cal. deg.$^{-1}$) |
|---|---|---|---|
| Toluene | $27{\cdot}4 \pm 0{\cdot}6$ | $5{\cdot}3 \times 10^{14}$ | $8 \pm 2$ |
| Nitromethane | $28 \pm 1$ | $1{\cdot}1 \times 10^{15}$ | $10 \pm 3$ |
| Nitrobenzene | $27 \pm 1$ | $2{\cdot}2 \times 10^{14}$ | $7 \pm 3$ |
| Acetic acid | $27 \pm 1$ | $2{\cdot}7 \times 10^{14}$ | $7 \pm 3$ |
| *n*-Propyl alcohol | $31 \pm 2$ | $1{\cdot}1 \times 10^{17}$ | $19 \pm 6$ |

TABLE 8. *Decomposition of* $p$-X·C$_6$H$_4$·N:N·CPh$_3$ *in toluene.*

| X | $E$ (kcal. mole$^{-1}$) | $B$ | $\Delta S^*$ (cal. deg.$^{-1}$) |
|---|---|---|---|
| Me | $25{\cdot}2 \pm 0{\cdot}6$ | $1{\cdot}95 \times 10^{13}$ | $2 \pm 2$ |
| Cl | $27{\cdot}3 \pm 0{\cdot}6$ | $2{\cdot}2 \times 10^{14}$ | $7 \pm 2$ |
| Br | $27{\cdot}8 \pm 0{\cdot}6$ | $4{\cdot}2 \times 10^{14}$ | $8 \pm 2$ |
| NO$_2$ | $29{\cdot}3 \pm 0{\cdot}6$ | $2{\cdot}1 \times 10^{15}$ | $11 \pm 2$ |

TABLE 9. *Decomposition of* $m$-X·C$_6$H$_4$·N:N·CPh$_3$ *in toluene.*

| X | $E$ (kcal. mole$^{-1}$) | $B$ | $\Delta S^*$ (cal. deg.$^{-1}$) |
|---|---|---|---|
| Me | $29{\cdot}2 \pm 0{\cdot}6$ | $8{\cdot}7 \times 10^{15}$ | $14 \pm 2$ |
| Cl | $29{\cdot}8 \pm 0{\cdot}6$ | $8{\cdot}8 \times 10^{15}$ | $14 \pm 2$ |
| NO$_2$ | $30{\cdot}5 \pm 0{\cdot}6$ | $1{\cdot}23 \times 10^{16}$ | $15 \pm 2$ |

TABLE 10. *Decomposition of* Ph·N:N·C(C$_6$H$_4$X-$p$)$_3$ *in toluene.*

| X | $E$ (kcal. mole$^{-1}$) | $B$ | $\Delta S^*$ (cal. deg.$^{-1}$) |
|---|---|---|---|
| Me | $27{\cdot}5 \pm 0{\cdot}6$ | $6{\cdot}3 \times 10^{14}$ | $9 \pm 2$ |
| Cl | $26{\cdot}0 \pm 0{\cdot}6$ | $1{\cdot}7 \times 10^{14}$ | $6 \pm 2$ |

*Mechanism of the Decomposition.*—The results presented in Table 2, and those of Cohen and Wang,[12] indicate that the rate of decomposition is independent of the initial concentration of phenylazotriphenylmethane, and that the first-order kinetic law is strictly obeyed. Huisgen and Nakaten,[10] by their discovery that neither chain-inhibitors nor chain-initiators affect the reaction, have demonstrated that no chain reaction is involved. It is therefore apparent that the reaction is kinetically of the first-order and is unimolecular. The results of the decomposition of phenylazotriphenylmethane in the presence of iodine show that the kinetics are unaffected by the nature of the subsequent reactions undergone by the free radicals, and so the rate of the reaction must be determined by homolytic dissociation into free radicals and nitrogen. The products of the decomposition in aromatic solvents indicate that under these conditions the aryl radicals react with the solvent by substitution, and the hydrogen atoms so formed react subsequently with any reducible species which may be present. Triphenylmethyl radicals fall into this category, and hence triphenylmethane is a major product. This does not, however, eliminate the possibility that reduction products of the other species present may not be formed; thus, for example, a little aniline is formed from the decompositon in nitrobenzene. Such products, however, would be expected only in small amount, since the highly reactive triphenylmethyl radicals may be present at appreciable concentrations.

It is of interest to examine the order of bond-fission in the decomposition. It is possible that both bonds may be broken simultaneously in a single rate-determining stage, or that they are broken successively in a two-stage process, of which one stage is rate-determining. Wieland, vom Hove, and Börner,[16] and Wieland, Hintermaier, and Dennstedt,[18] have shown that benzoylazotriphenylmethane decomposes more readily than phenylazotriphenylmethane, producing up to 70% of benzoyltriphenylmethane together with some *p*-benzoyltriphenylmethyl. Wieland, Ploetz, and Indest [19] have shown that a small amount of benzoylhydrazine is also produced in this reaction, and that the yield of nitrogen is not quantitative. The mechanism of this reaction was discussed earlier in this paper, and in the light of that discussion, it is difficult to imagine any route whereby benzoylhydrazine might be formed, other than the reduction of benzoylazo-radicals (Ph·CO·N:N·) by hydrogen atoms resulting from the reaction of benzoyl radicals with triphenylmethyl, yielding *p*-benzoyltriphenylmethyl and hydrogen. It is apparent, therefore, that the decomposition of benzoylazotriphenylmethane is a two-stage process, and that the nitrogen–triphenylmethyl bond is the first to break, producing the radicals Ph·CO·N:N· and $\cdot CPh_3$. The former radicals must be assumed to be sufficiently stable to permit the reduction of a few radicals before decomposition. An examination of the relative stability of azobenzene, benzoylazobenzene, and azodibenzoyl (Table 1) reveals that the ease of decomposition increases in that order, and indicates that the bond Ph–N is stronger than Ph·CO–N. When considered in conjunction with the above conception of the decomposition of benzoylazotriphenylmethane, this fact suggests that the decomposition of arylazotriarylmethanes proceeds along an analogous route [eqns. (9) and (10)] :

$$Ph\cdot N{:}N\cdot CPh_3 \longrightarrow Ph\cdot N{:}N\cdot + \cdot CPh_3 \quad . \; . \; . \; . \; . \; . \; . \; . \quad (9)$$

$$Ph\cdot N{:}N\cdot \longrightarrow Ph\cdot + N_2 \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad (10)$$

Nitrogen evolution in this reaction is, however, quantitative, and no products derived from the phenylazo-radical (Ph·N:N·) have been isolated. This is an indication that the second stage of the above scheme is very rapid, and hence it is the first stage which must be rate-determining. Such a view of the reaction is consistent with the effects of substituents in the phenyl group of phenylazotriphenylmethane, and this consistency lends additional support to the view of the reaction which has been developed.

*Solvent Effects.*—The most striking feature of the effects of changes of solvent on the Arrhenius parameters for the decomposition of phenylazotriphenylmethane (see Table 7; also Alder and Leffler [13] and Leffler and Hubbard [14]) is the parallelism exhibited between the energies and entropies of activation. The variations in energy of activation are compensated by the variations in entropy of activation, and only a very small and irregular solvent effect on the rate of reaction results (see Table 3). Parallel variation of $E$ and $\Delta S^*$ has been observed in the past in other reactions (see, for example, Fairclough and Hinshelwood,[33] and Raine and Hinshelwood [34]), and has been discussed by Ingold.[35] The last-named author points out that solvation of an ion or molecule must lead to stabilisation, since work is done by the molecule in orientating itself and attracting the molecules

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[33] Fairclough and Hinshelwood, *J.*, 1938, 236.

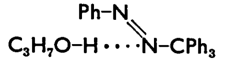
[34] Raine and Hinshelwood, *J.*, 1939, 1378.

[35] Ingold, " Structure and Mechanism in Organic Chemistry," Cornell Univ. Press, Ithaca, New York, 1953, p. 345.

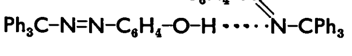
of the solvent. It follows that a change from a less polar to a more polar solvent should decrease or increase the activation energy of a reaction according as the transition state is more or less polar than the reactants. There may be compensating changes of entropy, for solvation, although it reduces energy, may increase the organisation of solvent molecules, thereby decreasing the probability of the solvated state. Thus, for example, in the present reaction, if the formation of the activated complex is accompanied by desolvation, then a change of solvent to one in which the extent of desolvation is greater must involve an increase in the energy of activation, and probably a parallel increase in the entropy of activation, since an increase in the degree of solvation must certainly result in the restriction of the " freedom " of the reacting molecules.

Neglecting, for the moment, the values of $E$ and $\Delta S^*$ obtained for the reaction in *n*-propyl alcohol, it is apparent from the results recorded in Table 7 that the above argument may be applied to the present example since, although the errors involved are large compared with the differences in the parameters, the values of $E$ and $\Delta S^*$ for nitromethane, which possesses the highest dielectric constant for the solvents used, are markedly greater than those for nitrobenzene, toluene, and acetic acid. Thus the values of $E$ and $\Delta S^*$ both increase with the capacity of the solvent for solvation. This conclusion is supported by the work of Alder and Leffler [13] and of Leffler and Hubbard.[14] It is apparent, therefore, that the transition state is solvated less than the initial state.

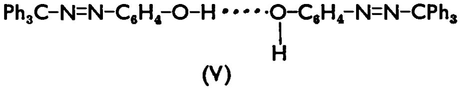
The results obtained for *n*-propyl alcohol are anomalous in that although the dielectric constant of this solvent is lower than that of nitromethane, both the energy and the entropy of activation are greater. Alcohols have in the past been found to be more efficient solvating solvents than aprotic solvents (see, for example, Hughes and Whittingham, quoted by Ingold,[36] who found that the rate of the reaction between trimethylamine and trimethylsulphonium ions varied with the solvent in the order $H_2O < MeOH < EtOH < Me{\cdot}NO_2$, in which the alcohols appear as intermediate with regard to their solvating properties between water and nitromethane). In the present instance the high degree of solvation of phenylazotriphenylmethane by *n*-propyl alcohol may be due to the formation of a hydrogen bond between the alcohol and one of the nitrogen atoms of phenylazotriphenylmethane (III). If the process of activation involves breaking this bond, an increase in activation energy of the required order should be observed. The formation of a hydrogen bond in the intial state would also explain the high value of $E$ (30 kcal. mole$^{-1}$) obtained by Huisgen and Nakaten [10] for the decomposition of phenylazotriphenylmethane in aniline, and such an explanation has been suggested by these authors. It is also possible that the abnormally high values obtained by Cohen and Wang [12] for the activation energies of the decomposition of *p*-hydroxyphenylazotriphenylmethane in toluene, acetic acid, and pyridine may be due to the formation of hydrogen bonds between two molecules of *p*-hydroxyphenylazotriphenylmethane, giving complexes of the types of (IV) and (V) :



(III)



(IV)



$Ph_3C-N=N-C_6H_4-O-H\cdots\cdots\underset{\displaystyle H}{\underset{|}{O}}-C_6H_4-N=N-CPh_3$

(V)

In addition to the contributions of these structures, the value of $E$ for the decomposition in pyridine may also be influenced by structure (VI). Similar considerations may also be

$$Ph_3C{\cdot}N{:}N-C_6H_4-O-H\cdots\cdots NC_5H_5$$

(VI)

applied to the decomposition of *p*-acetamidophenylazotriphenylmethane. The activation energy in this case is 30 kcal. mole$^{-1}$, and the high value may be attributed to the formation of hydrogen bonds between the –NH– group of one molecule and either the azo- or the carbonyl group of another.

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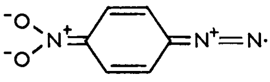
[36] Ref. 35, p. 350.

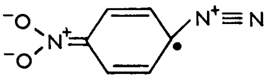
The formation of hydrogen-bonded complexes of this type must necessarily lead to an increase, not only in the energy, but also in the entropy of activation, since it must result in a certain restriction in the randomness of distribution and orientation of the reacting molecules. This expectation is also fulfilled by the evidence available.

The formation of complexes between reagent and solvent by the influence of electrostatic forces has been used by Cohen, Leffler, and Barbato [15] to explain their otherwise anomalous results concerning the decomposition of *p*-nitrophenylazotri-*p*-methoxyphenylmethane in benzonitrile and veratrole.

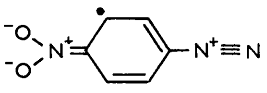
*Substituent Effects.*—The results given in Tables 8 and 4, and those of Cohen and Wang [12] show that, so far as is known, all substituent groups except methyl, when present in the *para*-position of the single phenyl nucleus, increase both the energy and the entropy of activation, and that these increases tend to compensate each other, as in the case of solvent variation, so that, in the temperature range studied, these various compounds all decompose at comparable rates. The lack of any simple relation between the polar characteristics of the substituent groups and their effect on the activation parameters indicates that these groups must be capable of influencing the reaction in more than one way. Cohen and Wang [12] attempted to explain the increase in activation energy occasioned by both electron-attracting and electron-repelling groups as being due to the stabilisation of the initial states by resonance in the presence of substituents of both types. However, there seems to be no reason why this effect should not work in the opposite direction, since an even greater stabilisation of the arylazo-radicals resulting from the primary dissociation, and hence of the transition state for the dissociation, would be expected by virtue of the contribution of canonical forms of the types (VII), (VIII), and (IX) in the presence of substituents having $-T$ effects, such as the nitro-group, and (X) and (XI) in the presence of substituents which display $+T$ effects, such as the methoxy-group. In any event, such an explanation, while it obviously must play a part, cannot be sufficient to explain the whole observed series of substituent effects, especially when the substituents are orientated *meta* to the azo-group, when canonical structures of this type cannot be written, and no stabilisation of either the initial or the transition state by resonance involving the substituent group is possible. There must therefore be a further mechanism whereby any substituent present can influence the activation parameters.



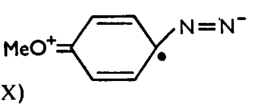
(VII)



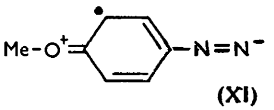
(VIII)



(IX)



(X)



(XI)

It is clear from the above consideration of solvent effects that the degree of desolvation which accompanies the formation of the transition state must exert a considerable influence on the activation parameters. The greater the extent of solvation of the initial state, the greater will be the desolvation which may take place, and hence the greater the increase in $E$ and $\Delta S^*$ which is occasioned. Thus it seems likely that a correlation should exist between the effect of a substituent on the degree of solvation of the reagent, by virtue of its effect on the polarisation of the reagent, and its effect on the activation parameters.

A detailed consideration of the effects of substituents on the solvation of arylazotriarylmethanes presupposes a knowledge of the magnitude and direction of the dipole moment of phenylazotriphenylmethane. This compound would be expected to possess a dipole moment, because Bergmann, Engel, and Wolff [37] have found that the dipole moment of triphenylmethane in carbon disulphide solution has the value 0·62 D. Moreover, an

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[37] Bergmann, Engel, and Wolff, *Z. phys. Chem.*, 1932, **17**, *B*, 81.

indication of the polarity of the Ph–N=N system is provided by the dipole moment of *cis*-azobenzene, which has been given [38] as 3·0 D. However, in molecules of this type, where the dipolar centres are widely separated, it is not certain that the total dipole moment should provide a good indication of the extent of the solvation, since it may well be that the dipolar centres are solvated separately. Hence it appears that reliable prediction of the solvation of these molecules is not possible.

Since the effects of substituents in the *para*-position are complicated by resonance stabilisation, which must take place to an uncertain extent, of initial and transition states, it seems likely that the solvation effects might be better illustrated by the *meta*-substituted compounds, in which the resonance effects are minimised. If the above discussion is essentially correct, the effects of *meta*-substituents should therefore depend only on solvation phenomena. The kinetic results given in Table 9 demonstrate that the energy and entropy of activation are increased by both electron-attracting and electron-repelling groups in the *meta*-position. Thus it seems likely that the solvation of the reagent molecule is increased by substituents of both polar types, and that the effect varies in the order $Me < Cl < NO_2$. This may be due to the separate solvation of the various polar centres in the molecule but, in any case, as is pointed out above, detailed discussion of the factors governing the solvation of such large molecules is, at present, unprofitable.

If it be now assumed that a similar influence on solvation is exerted by these groups when present in the *para*-position, the kinetic results for the decomposition of *para*-substituted arylazotriphenylmethanes can be rationalised if allowance is made for the resonance effects which may now come into play. The results given in Table 8 show that the activation parameters are decreased by the introduction of a *para*-methyl group, virtually unaffected by chlorine and bromine, but increased by the nitro-group in this position. Thus the solvation effect of the methyl group, which, in the *meta*-series exerts the smallest effect, must be counterbalanced by the resonance effect. In the case of the *p*-halogen-substituted compounds in which the solvation effect is expected to be somewhat larger, the two effects balance each other almost exactly, while the highly polar nitro-group exerts a large effect on the solvation, which is not balanced by the resonance effect.

In the series of compounds with substituents in the *para*-positions of the triphenylmethyl group it appears, on the other hand, that resonance is the major factor governing the stability of the compounds. This is not unreasonable, since *para*-substituents are known to exert a profound influence on the dissociation of hexa-arylethanes. Thus hexa-*p*-nitrophenylethane is completely dissociated into free radicals at 5° in benzene solution (Ziegler, quoted by Waters [39]). The results given in Table 10 show that methyl groups in this position exert very little influence on the kinetics of the decomposition and this may be due to the compensation of small resonance and solvation effects. The resonance effect of a halogen substituent might be expected to be larger, and it may be seen that a decrease in stability results from the introduction of *p*-chloro-substituents. The failure to prepare the corresponding bromo- and nitro-compounds suggests that in these compounds the resonance effect plays an even greater part, resulting in still less stable molecules which decompose under the conditions of their preparation.

It is emphasised that the above qualitative discussion is no more than an enumeration of factors which may contribute to the stability of arylazotriarylmethanes, and an attempt to show that, if certain not unreasonable assumptions are made, the influences revealed by the measurement of the activation parameters for the decomposition can be seen to fall into a rational pattern.

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King's College (University of London),
Strand, London, W.C.2.

[*Received, May 24th,* 1956.]

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[38] Hartley and Le Fèvre, *J.*, 1939, 531.

[39] Ref. 31, p. 53.