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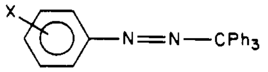
One-Bond Azo Initiators. Thermal Decomposition of Substituted (Phenylazo)triphenylmethanes[1,2]

Robert C. Neuman, Jr.,* and George D. Lockyer, Jr.[3]

Contribution from the Department of Chemistry, University of California, Riverside, California 92521. *Received October 25, 1982*

Abstract: Rate constants for thermal decomposition of the *p*-NO_2, *m*-NO_2, *m*-methyl, *p*-methyl, and unsubstituted (phenylazo)triphenylmethane (**1**) in octane and several aromatic solvents have been determined and correlated with medium viscosity. Decomposition rate constants for *p*-NO_2 and unsubstituted **1** in *n*-alkane solvents previously reported have been reanalyzed. These data indicate that β scission of intermediate diazenyl radicals is an important process in *n*-alkane solvents and becomes more important as increasing viscosity retards separative diffusion. However, β scission is not an important process in the aromatic solvents. Pressure severely retards the decomposition rates of *p*-NO_2 and unsubstituted **1** in octane, cumene, and *tert*-butylbenzene, giving activation volumes of +16 to +21 cm³/mol. Comparison of these pressure data with atmospheric pressure data gives activation volumes for formation and recombination of diazenyl radical–triphenylmethyl radical pairs. Problems associated with Hammett correlations of decomposition rates of the variously substituted compounds **1** are discussed.

The unsymmetrical (phenylazo)triphenylmethanes (**1**) are



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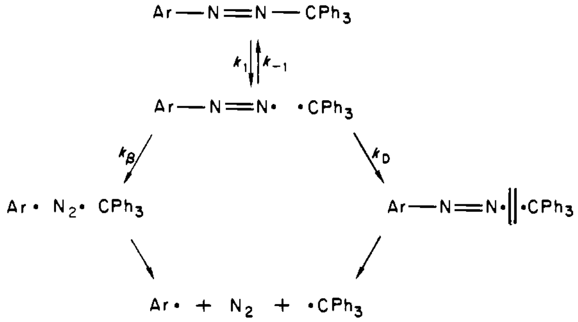
straightforward examples of azo initiators which decompose by stepwise scission of the C–N bonds (so-called "one-bond scission") (Scheme I). Pryor showed that the decomposition rates of both the parent compound (phenylazo)triphenylmethane (PAT) and its *p*-nitro derivative (*p*-NAT) decreased with increasing viscosity in a series of *n*-alkane solvents.[4] We showed that a substantial rate decrease also occurred upon application of high pressure to decomposing solutions of *p*-NAT in several hydrocarbon solvents.[5] The large observed decomposition activation volumes from this latter study, and Pryor's results, are strong evidence for the one-bond scission mechanism shown in Scheme I. CIDNP has also provided compelling evidence for the formation of the phenyldiazenyl radical (Ph—N=N·) from decomposition of similar unsymmetrical azo compounds.[6]

We now wish to report additional pressure studies on the unsubstituted azo compound (phenylazo)triphenylmethane (**1**, X = H) and the effect of a series of aromatic solvents on the decomposition rate constants for the unsubstituted, *p*-nitro, *m*-nitro, *p*-methyl, and *m*-methyl derivatives of **1**. These data, the earlier pressure studies, and those of Pryor provide a detailed picture of the reactivity of **1** and of the intermediate diazenyl radicals. In particular, it is clear that pressure effects cannot be simply attributed to viscosity variations and that there are distinct differences between aromatic and aliphatic solvents on the rates of decomposition of **1**. These data also require a reexamination of the question of substituent effects[7] on decomposition of **1**. Finally, we wish to point out that β scission of the intermediate diazenyl radicals in alkane solvents may be an important process.

Scheme I



Results and Discussion

Atmospheric Pressure Studies. Variously substituted (phenylazo)triphenylmethanes (**1**) were decomposed at atmospheric pressure in a series of aromatic solvents and in *n*-octane (Table I). On the basis of the mechanism in Scheme I, one would expect that the observed decomposition rates for **1** ($-\mathrm{d}(\mathbf{1})/\mathrm{d}t = k_0(\mathbf{1})$) would decrease with increasing medium viscosity if k_{-1} were competitive with k_D and if k_β were not substantially larger than k_D. Such a general trend is seen in the data for the aromatic solvents with the exception of the data for benzene.

A number of years ago, Pryor suggested that there should be a linear relationship between the reciprocal of the observed decomposition rate for one-bond scission initiators and a solvent viscosity function $(\eta/A_v)^\alpha$ (eq 1).[4] The term A_v is obtained from

$$1/k_0 = C(\eta/A_v)^\alpha \tag{1}$$

the Arrhenius equation for viscous flow ($\eta = A_v e^{E_v/RT}$) and α is an adjustable parameter. He found that this relationship reasonably fit his data for (phenylazo)triphenylmethane (PAT) and its *p*-nitro derivative (*p*-NAT) in a number of *n*-alkane solvents with an $\alpha = 0.5$. This relationship also fits our data in the aromatic solvents reasonably well and removes the discontinuity in the viscosity-rate correlation observed for benzene (Figure 1).[8]

The decomposition rate constants for the compounds **1** in *n*-octane (Table I), however, are significantly smaller than would be predicted by the viscosity correlation in the aromatic solvents. Our results for *p*-NAT (60 °C) in the aromatic solvents are contrasted with those for *p*-NAT (60 °C) in a series of *n*-alkanes

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[1] High-Pressure Studies. 25. Part 24: Neuman, R. C., Jr.; Binegar, G. A. *J. Am. Chem. Soc.* **1983**, *105*, 134.

[2] Presented at Pacific Conference on Chemistry and Spectroscopy, San Francisco, CA, October 27, 1982, paper 19, by Neuman, R. C., Jr.; Lockyer, G. D., Jr.

[3] (a) Taken from the Ph.D dissertation of G. D. Lockyer, Jr., University of California, Riverside, CA; June, 1975. (b) Present address: Buffalo Research Laboratory, Allied Chemical: Buffalo, New York.

[4] Pryor, W. A.; Smith, K. *J. Am. Chem. Soc.* **1970**, *92*, 5403.

[5] Neuman, R. C., Jr.; Lockyer, G. D., Jr.; Amrich, M. J., Jr. *Tetrahedron Lett.* **1972**, 1221.

[6] (a) Porter, N. A.; Marnett, L. J. *J. Am. Chem. Soc.* **1973**, *95*, 4361. (b) Porter, N. A.; Dubay, G. R.; Green, J. G. *Ibid.* **1978**, *100*, 920.

[7] (a) Cohen, S. G.; Wang, C. H. *J. Am. Chem. Soc.* **1953**, *75*, 5504. (b) Davies, G. L.; Hey, D. H.; Williams, G. H. *J. Chem. Soc.* **1956**, 4397. (c) Solomon, S.; Wang, C. H.; Cohen, S. G. *J. Am. Chem. Soc.* **1957**, *79*, 4104.

[8] This plot uses $\alpha = 0.64$ rather than $\alpha = 0.50$. The reason for this will be given later in the text. In any case, the graphs appear qualitatively similar with either value of α.

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Table I. Rate Constants for Decomposition of Substituted (Phenylazo)triphenylmethanes (1) in Several Solvents[a]

			$10^5 k_0$, s^{-1}				
			60 °C		50 °C		
solvent	η,[b] cP	$10^2 A_v$[b]	*p*-NO_2	*m*-NO_2	H	*m*-Me	*p*-Me
octane	0.395[c]	1.592[c]	9.97 ± 0.01	10.1 ± 0.8	15.9 ± 0.4	(8.9 ± 0.7)[d]	(8.6 ± 0.5)[d]
toluene	0.418	1.491	13.6 ± 0.1 (1.60 ± 0.01)[d]	12.2 ± 0.1 (1.25 ± 0.04)[d]	17.3 ± 0.1 (9.23 ± 0.08)[d]	18.1 ± 0.1 (9.74 ± 0.01)[d]	15.2 ± 0.1 (9.3 ± 0.4)[d]
benzene	0.435	0.884	10.9 ± 0.1	9.92 ± 0.1	13.7 ± 0.1	13.0 ± 0.1	12.6 ± 0.1
ethylbenzene	0.480	1.645	12.7 ± 0.1	11.0 ± 0.1	15.8 ± 0.1	17.2 ± 0.1	16.2 ± 0.2
cumene	0.543	1.355	11.5 ± 0.1	10.4 ± 0.1	15.0 ± 0.1	15.1 ± 0.1	14.0 ± 0.1
tert-butylbenzene	0.758[e]	1.256[e]	9.7 ± 0.14	9.18 ± 0.04	13.3 ± 0.1	13.0 ± 0.1	13.5 ± 0.2

[a] Determined by monitoring evolution of dinitrogen gas. [b] At 50 °C; Rossini, F. D. "Selected Values of Properties of Hydrocarbons and Related Compounds"; American Petroleum Institute Research Project 44; Carnegie University Press; New York, 1952. [c] Reference 9. [d] At 45.0 °C. [e] Determined in this study.

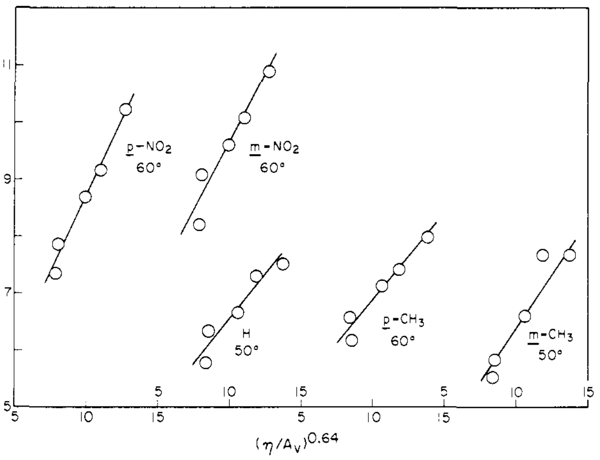

Figure 1. Dependence of $1/k_0$ on the viscosity function $(\eta/A_v)^{0.64}$ for compounds **1** (X shown on figure) in aromatic solvents.

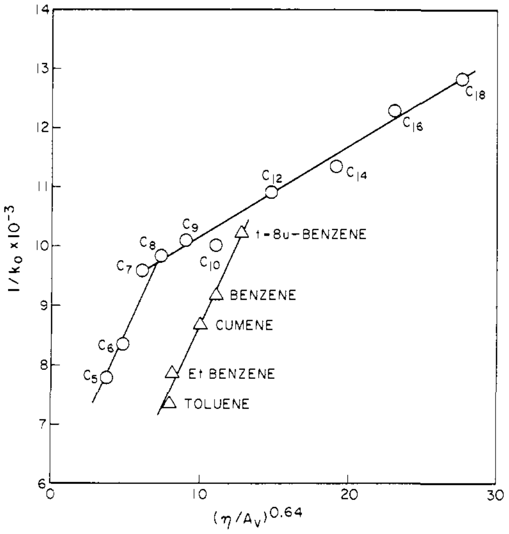

Figure 2. Dependence of $1/k_0$ on the viscosity function $(\eta/A_v)^{0.64}$ for ((*p*-nitrophenyl)azo)triphenylmethane (60°) in alkane (○) and aromatic (△) solvents.

(Figure 2).[4,9] It is clear that not only for *n*-octane but for all the alkanes C_5–C_{10}, the apparent decomposition rate constants for *p*-NAT are smaller than those in the aromatic solvents of comparable viscosity (or more properly η/A_v).[8] We suggest that the origin of this difference is a specific solvent effect on both the primary scission step (k_1, Scheme I) and the β-scission step (k_β, Scheme I). This will be discussed in more detail below.

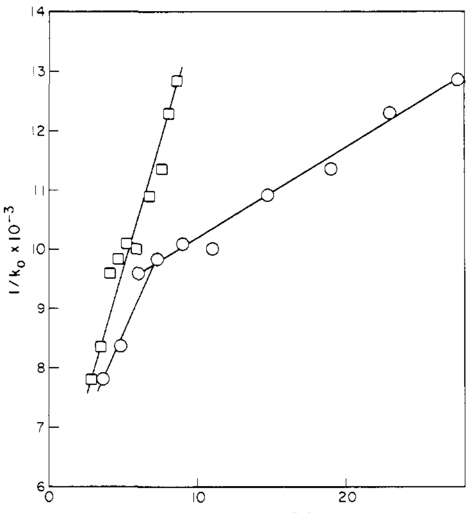

Figure 3. A comparison of the dependence of $1/k_0$ on the viscosity function $(\eta/A_v)^{0.64}$ (○) and on the viscosity function of f(η) (□) (see text) for ((*p*-nitrophenyl)azo)triphenylmethane in alkane solvents (60 °C).

The complete kinetic expressions for k_0 and $1/k_0$ are those given in eq 2 and 3, respectively (Scheme I). Using Pryor's proposal that $k_D = A_D\,(A_v/\eta)^\alpha$, the expression for $1/k_0$ shown in eq 4 is obtained. Thus, the plots in Figures 1 and 2 would be expected to be linear only if $k_\beta/k_D \ll 1$ (see eq 3)

$$k_0 = k_1[(k_D + k_\beta)/(k_{-1} + k_D + k_\beta)] \qquad (2)$$

$$1/k_0 = [k_{-1}/(k_1 k_D)][1/(1 + k_\beta/k_D)] + 1/k_1 \qquad (3)$$

$$1/k_0 = [k_{-1}/k_1 A_D][\eta/A_v]^\alpha[1/(1 + (k_\beta/A_D)(\eta/A_v)^\alpha)] + 1/k_1 \qquad (4)$$

Within experimental error, the data points in the aromatic solvents appear to define a straight line and so do the alkane solvent data from C_7–C_{18}. However, the data points for pentane and hexane fall off of the latter line. This same apparent curvature (or discontinuity) can be seen not only in these data for *p*-NAT at 60 °C but also in alkane data for *p*-NAT at 50 °C and PAT at 60 °C where pentane and/or hexane were used as low viscosity solvents.[4,9] If these low viscosity data points are accurate,[10] we suggest that this nonlinear appearance of the alkane data (see Figure 2) results from an effective competition between β scission of the initially formed diazenyl radical (k_β) and separative diffusion of this radical and triphenylmethyl from the initial solvent cage. To test this idea, we have used the complete eq 3 to analyze all of the data[4,9] for *p*-NAT at 50 and 60 °C and for PAT at 60 °C. The results derived from inclusion and exclusion of k_β in the analysis are contrasted for *p*-NAT (60 °C) in Figure 3.[8]

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(9) Also, see the Ph.D. dissertation of W. K. Smith, The Louisiana State University and Agricultural and Mechanical College, 1969; University Microfilms, Inc., Ann Arbor, MI.

(10) Pentane, unlike the other solvents, boils below the reaction temperatures. It is assumed that reactions in this solvent were carried out in sealed tubes. Values of η/A_v at both 50 and 60 °C for pentane were obtained[9] from extrapolation of data at lower temperatures using the equation $\eta/A_v = e^{E_v/RT}$.

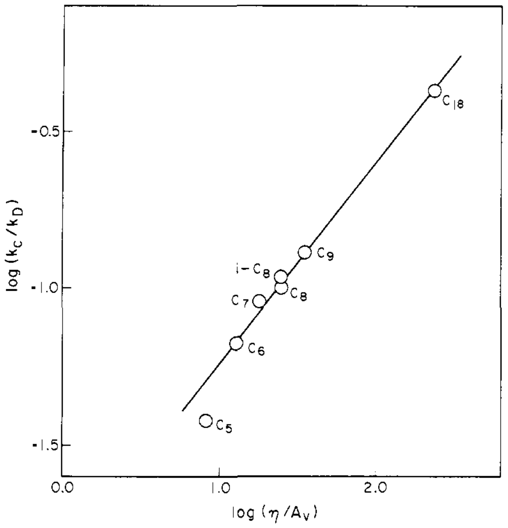

Figure 4. Dependence of log (k_c/k_D) for decomposition of di-*tert*-butyl hyponitrite (Traylor[12]) (45 °C) on the viscosity function log (η/A_v) in a series of alkane solvents.

Besides the fact that the discontinuity disappears, an additional satisfying aspect of including k_β in the alkane solvent analysis is that the viscosity dependence of $1/k_0$ in both alkane and aromatic solvents becomes much more similar (contrast Figures 2 and 3). While this is not required a priori, high-pressure results which will be reported later in this paper suggest that this should be the case.

In order to carry out this analysis, the assumption was made that $k_\beta/k_D \ll 1$ for the *low molecular weight* solvents. Thus, the initial slopes of plots of $1/k_0$ vs. $(\eta/A_v)^\alpha$ were calculated and assigned as the quantities k_{-1}/k_1A_D (see eq 4). An approximate value of $1/k_1$ was also calculated from the intercept of the line through the low molecular weight solvent data points. These "first-approximation" values of k_{-1}/k_1A_D and $1/k_1$ were then used in the full equation (eq 4) to numerically obtain a value of k_β/A_D for each pair of values of $1/k_0$ and $(\eta/A_v)^\alpha$. An average value of k_β/A_D was selected from the set of runs obtained for each system, and it was used to generate values for the function $[(\eta/A_v)^\alpha/(1 + (k_\beta/A_D)(\eta/A_v)^\alpha)]$ which we call f(η). Plots of $1/k_0$ vs. f(η) were made, and new values of k_{-1}/k_1A_D and $1/k_1$ were obtained as the slope and intercept of the best straight line through the data (see eq 4). The new slopes and intercepts were subsequently used to numerically recalculate values of k_β/A_D, and the whole process repeated until no further significant improvement was obtained. The results are shown for *p*-NAT at 60° in Figure 3.

For these analyses of the alkane solvent data we chose a value of 0.64 for α.[8] Pryor originally used an α value of 0.50, but later showed that values in the range of 0.70–0.75 were probably better.[11] Our intermediate value of 0.64 was obtained from a correlation of the viscosity function η/A_v with cage effect data determined by Traylor for relative rates of product formation from di-*tert*-butyl hyponitrite decompositions in a series of *n*-alkanes.[12] Thermal decomposition of di-*tert*-butyl hyponitrite gives a geminate aggregate of two *tert*-butoxy radicals and dinitrogen which then leads to di-*tert*-butyl peroxide by cage combination of the *tert*-butoxy radicals (k_c) and separatively diffused *tert*-butoxy radicals (k_D) which give *tert*-butyl alcohol by hydrogen abstraction from the alkane solvent. Assuming that the quantities k_c/k_D obtained from ratios of di-*tert*-butyl peroxide and *tert*-butyl alcohol depend on solvent viscosity in the manner described above (i.e., $k_c/k_D = k_c/A_D(A_v/\eta)^\alpha$) and that k_c does not depend on viscosity, we reasoned that a plot of log (k_c/k_D) vs. log (η/A_v) would be a straight line with a slope equal to α. That plot (Figure 4) gave a slope of 0.64. The deviation of the point for pentane may be significant, but it may also be a reflection of the very low cage effect in this solvent and the error in measuring the resultant large difference in relative yields of di-*tert*-butyl peroxide and *tert*-butyl alcohol.

Table II. Kinetic Data for the Decomposition of Substituted (Phenylazo)triphenylmethanes (1) at Atmospheric Pressure in Alkane Solvents

X	*T*, °C	solvent	10^4k_0,[a] s^{-1}	k_β/k_D	k_{-1}/k_D	f_r[b]
H	60	C_6	7.60	0.23	0.49	0.24
		C_7	6.60	0.29	0.62	0.34
		C_8	6.41	0.35	0.75	0.36
		C_{10}	5.72	0.52	1.13	0.43
		C_{12}	5.35	0.70	1.51	0.47
		C_{14}	4.99	0.91	1.96	0.50
		C_{16}	4.76	1.09	2.36	0.52
			$k_1 = 10.0 \times 10^{-4}$		$k_\beta/k_{-1} = 0.46$	
p-NO_2	50	C_5	0.360	0.26	0.55	0.10
		C_6	0.275	0.34	0.72	0.31
		C_7	0.242	0.43	0.91	0.40
		C_9	0.220	0.64	1.37	0.45
		C_{10}	0.202	0.79	1.69	0.50
		C_{12}	0.193	1.07	2.28	0.52
		C_{14}	0.187	1.41	2.99	0.53
		C_{16}	0.172	1.72	3.65	0.57
			$k_1 = 0.401 \times 10^{-4}$		$k_\beta/k_{-1} = 0.47$	
p-NO_2	60	C_5	1.280	0.29	0.58	0.31
		C_6	1.195	0.38	0.76	0.35
		C_7	1.043	0.48	0.95	0.44
		C_8	1.015	0.58	1.16	0.45
		C_9	0.990	0.71	1.42	0.47
		C_{10}	0.999	0.88	1.74	0.46
		C_{12}	0.917	1.17	2.32	0.50
		C_{14}	0.880	1.52	3.01	0.52
		C_{16}	0.813	1.83	3.63	0.56
		C_{18}	0.778	2.19	4.35	0.58
			$k_1 = 1.85 \times 10^{-4}$		$k_\beta/k_{-1} = 0.50$	

[a] From ref 4. [b] $f_r = 1 - (k_0/k_1)$; see ref 4.

The results of the complete analyses of the alkane solvent data using eq 4 which contains k_β are outlined in Table II. They suggest that k_β/k_D is significant and that β scission of initially formed phenyldiazenyl radicals is an important cage reaction. The values for k_1 calculated from these analyses lead to substantially larger values of f_r (fraction of diazenyl radicals returning to starting azo compound) than those previously reported.[4]

Use of the same procedure to analyze our data (Table I) for the variously substituted (phenylazo)triphenylmethanes in the aromatic solvents leads to the conclusion that k_β/k_D is insignificant in these solvents; i.e., β scission is apparently *not* an important cage process in aromatic solvents. The results of these analyses are given in Table III.[13]

Direct comparison between the aromatic and aliphatic solvent series is possible for ((*p*-nitrophenyl)azo)triphenylmethane because its decomposition was studied in both solvent series at the same temperature (60 °C). In addition to the difference in importance of β scission of the phenyldiazenyl radical, the inherent "zero viscosity" decomposition rate constant (k_1) is almost twice as large in the aromatic solvent series (3.38×10^{-4} s^{-1}) as in the *n*-alkanes (1.85×10^{-4} s^{-1}). We suggest that both of these observations reflect stabilization of phenyldiazenyl radicals by aromatic solvents. In contrast, the ratio k_{-1}/k_D does not seem to be much different in aromatic or aliphatic solvents of the same "viscosity". It increases linearly with the viscosity function $(\eta/A_v)^{0.64}$ (Figure 5). Either (1) k_{-1} and k_D do not depend on whether the solvent is aromatic or aliphatic or (2) both rate constants are affected to

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(11) (a) Pryor, W. A.; Morkved, E. H.; Bickley, H. T. *J. Org. Chem.* **1972**, *37*, 1999. (b) Lockyer[3] used a value of 0.75 for α in his original calculations.

(12) Kiefer, H.; Traylor, T. *J. Am. Chem. Soc.* **1967**, *89*, 6667.

(13) The value of 0.64 has been used for α for the series of aromatic solvents. While there is no firm experimental basis for this, the data do not appear qualitatively "better" in plots using somewhat larger or smaller α values. Variation of α does not affect the conclusion that k_β/k_D is insignificant for these systems.

Table III. Analysis of Kinetic Data for Decomposition of Substituted (Phenylazo)triphenylmethanes (1) in Aromatic Solvents

X	T, °C	solvent	10^4k,[a] s^{-1}	k_β/k_D	k_{-1}/k_D	f_r[c]
p-NO_2	60	toluene	1.36	b	1.49	0.60
		ethylbenzene	1.27		1.66	0.62
		cumene	1.15		1.94	0.66
		benzene	1.09		2.10	0.68
		tert-butylbenzene	0.977		2.46	0.71
		$k_1 = 3.38 \times 10^{-4}$				
m-NO_2	60	toluene	1.22	b	0.92	0.52
		ethylbenzene	1.10		1.13	0.53
		cumene	1.04		1.26	0.56
		benzene	0.992		1.37	0.58
		tert-butylbenzene	0.918		1.56	0.61
		$k_1 = 2.35 \times 10^{-4}$				
H	50	toluene	1.73	b	1.64	0.62
		ethylbenzene	1.58		1.89	0.65
		cumene	1.50		2.05	0.67
		benzene	1.37		2.33	0.70
		tert-butylbenzene	1.33		2.43	0.71
		$k_1 = 4.57 \times 10^{-4}$				
p-CH_3	50	toluene	1.52	b	1.79	0.64
		ethylbenzene	1.62		1.61	0.62
		cumene	1.40		2.03	0.67
		benzene	1.35		2.14	0.68
		tert-butylbenzene	1.26		2.36	0.70
		$k_1 = 4.24 \times 10^{-4}$				
m-CH_3	50	toluene	1.81	b	1.41	0.59
		ethylbenzene	1.71		1.55	0.61
		cumene	1.51		1.89	0.65
		benzene	1.30		2.35	0.70
		tert-butylbenzene	1.30		2.35	0.70
		$k_1 = 4.36 \times 10^{-4}$				

[a] From Table I. [b] Too small to determine. [c] $f_r = 1 - (k_0/k_1)$; see ref 4.

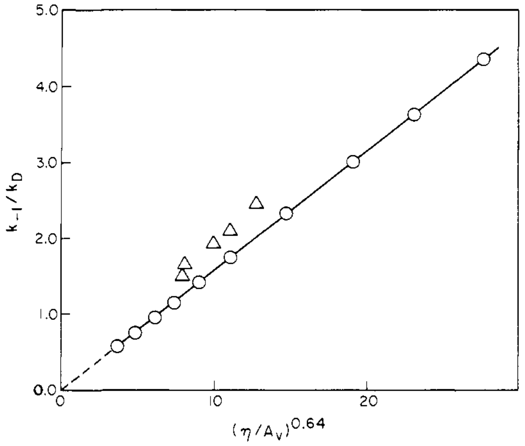

Figure 5. Dependence of k_{-1}/k_D on the viscosity function $(\eta/A_v)^{0.64}$ for ((p-nitrophenyl)azo)triphenylmethane in alkane (○) and aromatic (△) solvents.

about the same extent. The larger values of f_r for ((p-nitrophenyl)azo)triphenylmethane in the aromatic solvents are a result of the lesser importance of k_β in these solvents compared to the alkanes.

High-Pressure Studies. (Phenylazo)triphenylmethane and ((p-nitrophenyl)azo)triphenylmethane were decomposed in octane, cumene, and *tert*-butylbenzene at various pressures. As expected, pressure decreased the decomposition rate constants (Table IV) and the data give large positive activation volumes (Table V).

Large positive values of ΔV^* have come to be associated with one-bond scission of radical initiators followed by partial return of the primary cage radical products to starting initiator.[1,5,14] Part of this rate retardation arises from a pressure-induced increase in solvent viscosity.[15] However, in this case, it is not the only cause. Values of $1/k_0$ for decomposition of p-NAT in both aromatic and aliphatic solvents at atmospheric and high pressure are plotted as a function of viscosity in Figure 6. The rate retardation induced by pressure is clearly much greater than that resulting simply from changes in viscosity.

Table IV. Rate Constants for Decomposition of (Phenylazo)triphenylmethanes (1) in Various Solvents at High Pressure[a]

			10^5k_0, s^{-1}		
X	T, °C	P, atm	octane	cumene	*tert*-butylbenzene
H	50	1	15.3 ± 0.3	15.5 ± 1.0	14.3 ± 1.4
		1125	7.53 ± 0.19	6.82 ± 0.17	3.83 ± 0.29
		2125	4.05 ± 0.18	2.74 ± 0.07	2.50 ± 0.18
		3210	1.94 ± 0.08	1.61 ± 0.07	1.44 ± 0.04
		4210	1.17 ± 0.05	0.765 ± 0.06	0.953 ± 0.10
p-NO_2	60	1	11.4 ± 0.00	11.6 ± 0.2	10.3 ± 0.2
		1240	4.44 ± 0.03	4.73 ± 0.13	4.03 ± 0.09
		2110	2.56 ± 0.04	2.27 ± 0.05	2.07 ± 0.10
		3200	1.31 ± 0.01	1.22 ± 0.03	0.968 ± 0.047
		3840	0.832 ± 0.018	0.723 ± 0.031	0.444 ± 0.014

[a] Determined by monitoring UV absorption of the azo linkage.

Table V. Activation Volumes for Decomposition of Compounds 1 in Various Aromatic Solvents

X	T, °C	solvent	ΔV_0^*, cm^3/mol
H	50	octane	+16.4 ± 0.4
		cumene	+18.8 ± 1.0
		tert-butylbenzene	+16.5 ± 2.5
p-NO_2	60	octane	+17.8 ± 0.4
		cumene	+19.0 ± 0.6
		tert-butylbenzene	+21.1 ± 1.0

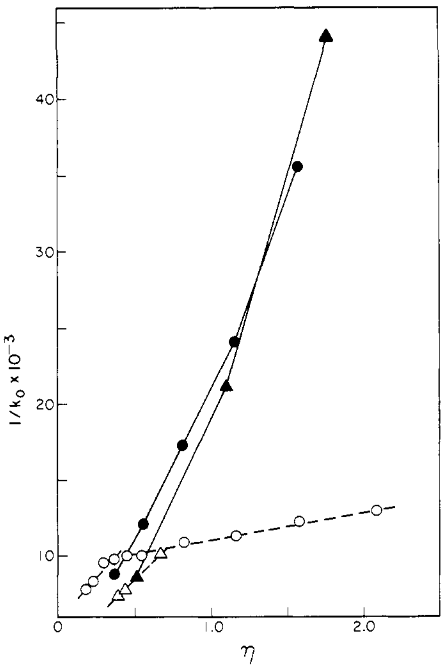

Figure 6. Dependence of $1/k_0$ on viscosity (η) for decomposition of ((p-nitrophenyl)azo)triphenylmethane in n-octane at different pressures (●), in cumene at different pressures (▲), in alkanes at atmospheric pressure (○), and in aromatic solvents at atmospheric pressure (△).

This observation is qualitatively consistent with expectation of effects of pressure as well as viscosity on the various rate constants included in the kinetic expression for $1/k_0$ (eq 3). Both pressure and solvent variation at atmospheric pressure lead to increases

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(14) Neuman, R. C., Jr. *Acc. Chem. Res.* **1972**, *5*, 381.

(15) Neuman, R. C., Jr.; Bussey, R. J. *J. Am. Chem. Soc.* **1970**, *92*, 2440.

Table VI. Activation Volumes (cm^3/mol) Derived from Equation 5

ΔV_{-1}*	ΔV_1*
−5.0	+9.8
−10.0	+6.1
−15.0	+2.4

in viscosity, resulting in decreases in k_D and increases in $1/k_0$. However, pressure, but not viscosity, should decrease the rate constants of the homolytic scission reactions (k_1 and k_β) and increase that for radical combination (k_{-1}). These changes are predicted to additionally increase $1/k_0$.

At this point it should be noted how similarly the pressure data in octane and cumene vary with viscosity, in contrast to the previously discussed dissimilar behavior of the atmospheric pressure data in the alkanes and aromatics (Figure 6). We believe that this is because pressure has a substantial retarding effect on the β-scission process which we have proposed is important in the alkanes but unimportant in the aromatics (vide supra) and that these pressure results thus provide additional support for our earlier analysis.

Since k_β is not important in the aromatic solvent systems, the simpler kinetic expression (eq 5) derived from eq 4 by neglecting

$$k_1/k_0 = k_{-1}/k_D + 1 \qquad (5)$$

k_β/k_D makes it possible to analyze the cumene pressure results in more detail. The form of equation 5 useful for analyzing the high pressure results is shown in eq 6.[16] By appropriate substitution of known quantities as follows, this equation provides a relationship between ΔV_1* and ΔV_{-1}*.

$$(k_1/k_{0,p})e^{-\Delta V_1 * P/RT} = (k_{-1}/k_D)e^{-\Delta V_{-1} * P/RT} + 1 \qquad (6)$$

The basic premise for using eq 6 is that *at the same value of* η *and* T the values of k_1 and k_{-1}/k_D derived from the atmospheric pressure aromatic solvent data for *p*-NAT (Table III and Figure 6) can be used in conjunction with the value of k_0 at pressure P in the solvent cumene for *p*-NAT (Table IV and Figure 6).[17,18] The resulting relationship, $4.120e^{-0.01302\Delta V_1 *} = 2.463e^{-0.01302\Delta V_{-1} *} + 1$, gives the series of values for ΔV_1* shown in Table VI for a chosen set of values of ΔV_{-1}*. Gratifyingly, negative values of ΔV_{-1}* give positive values of ΔV_1*, and their range is quite reasonable on the basis of our experience. For example, we have shown that activation volumes for homolytic scission (ΔV_1*) are about +5 cm^3/mol for a variety of systems[14,19,20] and activation volumes for radical combination (ΔF_{-1}*) can be expected to be in the range of −5 to −10 cm^3/mol,[15,21] both consistent with the results in Table VI.

Substituent Effects. The above considerations suggest that effects of ring substituents on decomposition of (phenylazo)triphenylmethane should be evaluated from linear free energy correlatiaons of the primary homolytic scission rate constrants k_1. Previous workers have considered only k_0 values.[7] Unfortunately, no complete set of values of k_1 exists at any single temperature. However, a set of values of k_0 has been determined in toluene at 45 °C for the five compounds used in this study (Table I). Since the ratios k_1/k_0 which can be calculated from our data are relatively insensitive to temperature (see Table II, data for *p*-NAT in alkanes at 50 and 60 °C), values of k_1 at 45 °C in toluene have been estimated by using the k_1/k_0 ratios for the individual compounds in toluene at 50 or 60 °C in conjunction with the values of k_0 at 45 °C (Table I). Unfortunately, a Hammett plot of log k_1 (est) vs. σ is basically no different than that of a plot of log k_0 vs. σ (Figure 7). As demonstrated by other workers, electron-withdrawing substituents depress the rate (ρ = −1.0), but the overall correlation with σ is poor.[7] It is likely that the errors associated with extracting k_1 from the kinetic data are sufficiently large to mask trends which might be present. It is also possible that a combination of solvation and electronic effects is operating which preclude a good correlation.[7] In any case, our data shed no more light on these questions than those of past workers.

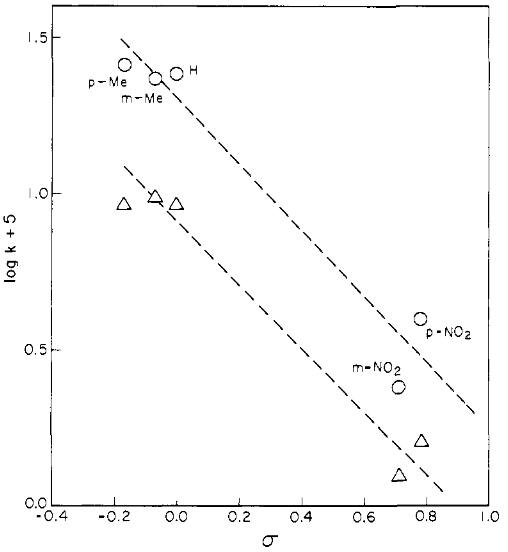

Figure 7. Hammett plot for the decomposition of ((*p*-nitrophenyl)azo)triphenylmethane in toluene at 45 °C; log k_0 (△), log k_1 (est) (○).

Experimental Section

Solvents. The solvents used in the kinetic studies *n*-octane (Phillips "pure" grade), benzene (Mallinckrodt AR), toluene (Mallinckrodt AR), ethylbenzene (Matheson Coleman & Bell (MCB)) cumene (Aldrich and MCB), and *tert*-butylbenzene (Aldrich and MCB) were purified by the addition of successive 200-mL portions of concentrated sulfuric acid (Allied) to approximately 1-L portions of the solvent, with stirring, until the acid layer remained colorless upon stirring overnight. The solvents were then washed with saturated sodium bicarbonate solution (MCB), washed with distilled water, and dried with Drierite (W. A. Hammond Drierite Co.). The solvents were then distilled through a 12-in Vigreux column from potassium carbonate (Mallinckrodt) under an argon atmosphere. The solvents were stored in brown bottles, under argon and over Linde molecular sieve, 4A (Allied, B&A). All other solvents were reagent grade and were used as received.

((*p*-Nitrophenyl)azo)triphenylmethane (*p*-NAT).[4,7a] To 7.65 g (50.0 mmol) of (*p*-nitrophenyl)hydrazine (MCB) were added 250 mL of anhydrous diethyl ether (Mallinckrodt) and 6.99 g (25.1 mmol) of triphenylmethyl chloride (Aldrich). The mixture was refluxed for approximately 1 h, and (*p*-nitrophenyl)hydrazine hydrochloride was removed by filtration. The hydrochloride salt was washed with ether, the ether layers were combined, and the ether was removed under vacuum by rotary evaporation. The recovered *N*-(4-nitrophenyl)-*N′*-(triphenylmethyl)hydrazine was recrystallized from benzene (2.64 g, 6.78 mmol, 27%); mp 182–186 °C. This hydrazo compound was oxidized by its addition (1.63 g, 4.1 mmol) to 1.2 mL of isoamyl nitrite (MCB) (9 mmol) in ether followed by addition of two or three drops of propionyl chloride to initiate the reaction. The solution was refluxed two hours and allowed to stand overnight. Recrystallization of the crude azo compound from a 1:1 mixture of methylene chloride and low-boiling petroleum ether (30–60 °C) yielded needles of *p*-NAT (1.00 g, 2.54 mmol, 64%) mp 118–119 °C (lit.[7a] 118–119 °C).

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(16) This equation was derived from equation 5, by substituting $k_1e^{-\Delta V_1 * P/RT}$ for k_1 and $k_{-1}e^{-\Delta V_{-1} * P/RT}$ for k_{-1}. The quantity $k_{o,p}$ is the value of k_0 at pressure P, and k_D is assumed[15] to depend only on η whether at one atmosphere or at some other pressure P. Our previous observations are that pressure effects on k_D can be solely accounted for by viscosity changes induced by pressure.

(17) $k_1 = 3.38 \times 10^{-4}$ s^{-1}, *p*-NAT, 60 °C, aromatic solvent series, 1 atm; $k_{o,p} = 8.20 \times 10^{-5}$ s^{-1}, *p*-NAT, 60 °C, cumene at 356 atm (same viscosity as in *t*-butylbenzene at 1 atm);[18] $k_{-1}/k_D = 2.463$, *p*-NAT, 60 °C, *tert*-butylbenzene, 1 atm; $P = 356$ atm, $T = 333.2$ °C.

(18) Viscosity values for a number of hydrocarbon solvents at various pressures have been determined by: Bridgeman, P. "Collected Experimental Papers"; Harvard University Press: Cambridge, MA 1964; Vol. IV, p 2043.

(19) Neuman, R. C., Jr.; Amrich M. J., Jr. *J. Org. Chem.* **1980**, *45*, 4629.

(20) Neuman, R. C., Jr.; Amrich, M. J., Jr. *J. Am. Chem. Soc.* **1972**, *94*, 2730.

(21) (a) The first pressure study of (phenylazo)triphenylmethane was reported by Lamb 16 years ago.[21b] He found that pressure severely retarded the formation of iodobenzene when iodine was added to decomposing solutions of (phenylazo)triphenylmethane in methylcyclohexane. These data support our conclusions that k_β is competitive with k_D in alkanes. If $k_D >> k_\beta$, one would anticipate that most of the resulting phenyl radicals would be scavenged independent of pressure. (b) Lamb, R. C.; Pacifici, J. G. *J. Phys. Chem.* **1966**, *70*, 314.

((*m*-Nitrophenyl)azo)triphenylmethane (*m*-NAT). To 4.85 g (26 mmol) of the (*m*-nitrophenyl)hydrazine hydrochloride (Aldrich) was added 7.05 g (25 mmol) of triphenylmethyl chloride in 66 mL of dry pyridine (Aldrich) (dried over potassium hydroxide pellets), and the solution was stirred for 3 h.[7c] The pyridine hydrochloride was then removed and washed with pyridine, and the filtrate and pyridine wash were diluted with 250 mL of water. The resulting solid and ether extracts of the aqueous pyridine layer were combined, yielding 7.56 g of crude hydrazo compound (79%). This was dissolved in ether to which was added dropwise 9.0 mL of isoamyl nitrite followed by two or three drops propionyl chloride. The solution was refluxed for 2 h, the ether was removed, and 3.03 g crude azo compound was obtained (40%). Repeated crystallization from a mixture of methylene chloride and petroleum ether yielded 1.57 g of *m*-NAT (mp 111–112 °C (lit.[7c] 111–112 °C)).

((*p*-Tolyl)azo)triphenylmethane (*p*-TAT). (*p*-Tolylazo)triphenylmethane was prepared in the same manner as *m*-NAT. To 4.10 g (26 mmol) of the *p*-tolylhydrazine hydrochloride (Aldrich) and 8.00 g (30 mmol) triphenylmethyl chloride was added 80 mL pyridine, and 6.17 g crude hydrazo compound (68%) was obtained. Oxidation of this hydrazo compound with 9.0 mL of isoamyl nitrite produced 6.15 g crude azo compound which, upon repeated recrystallization, yielded 1.78 g of *p*-TAT (mp 104–105 °C (lit.[7c] 103 °C)).

((*m*-Tolyl)azo)triphenylmethane (*m*-TAT). (*m*-Tolylazo)triphenylmethane was produced by a method similar to the one used for *m*-NAT. To 4.10 g of *m*-tolylhydrazine hydrochloride (Aldrich) was added 8.52 g of triphenylmethyl chloride in 80 mL of dry pyridine. The crude hydrazo compound product (8.52 g, 93%) was treated with 10.5 mL of isoamyl nitrite to yield 6.81 g of crude azo compound (74%). Upon repeated recrystallization from a mixture of methylene chloride and petroleum ether, 1.98 g of *m*-TAT resulted (mp 108–109 °C (lit.[7c] 108–109 °C)).

(Phenylazo)triphenylmethane (PAT). (Phenylazo)triphenylmethane was obtained from Eastman Organic Chemicals and was recrystallized from benzene prior to use (mp 111–112 °C (lit.[7a] 110–112 °C)).

Kinetics. The atmospheric pressure kinetics were followed by one of three methods. The first method, and that used most frequently, was the determination of the rate of azo compound decomposition by monitoring the rate at which nitrogen was evolved.[22] A 0.15–0.30-mmol sample of crystalline azo compound was added to the sample cell, followed by addition of 10 mL of the appropriate solvent. The constant temperature bath (Precision Scientific) was attached, and the system was deoxygenated and adjusted to atmospheric pressure by using nitrogen gas. After a temperature equilibration period of 10 min, the volume of nitrogen gas evolved was monitored vs. time.

The second method used for the determination of the decomposition rates for atmospheric pressure samples was the sealed ampule technique using UV–vis analysis of the reaction mixtures. Stock solutions of *p*-NAT had concentrations of 9.95×10^{-4} M in octane, 9.76×10^{-4} M in cumene, and 1.07×10^{-3} M in *tert*-butylbenzene. The PAT stock solutions had concentrations of 1.01×10^{-3} M in cumene and 9.97×10^{-4} M in *tert*-butylbenzene.

Samples of the stock solutions approximately 1 mL in volume were placed in Pyrex ampules (8-mm Pyrex tubing) which had been previously cleaned by soaking in 3:1 mixture of nitric and sulfuric acids, followed successively by ammonium hydroxide and distilled water and then, finally, by oven drying. Each run utilized eight samples. The samples were loaded into the ampules, the samples were degassed by three freeze–pump–thaw cycles, and the samples were sealed under vacuum. They were stored in the freezer (−15 °C) until use.

Decomposition of the samples was monitored via the absorbance of the azo linkage (–N=N–) which has an absorbance maximum at 440 nm for *p*-NAT ($\epsilon \sim 200$) and a maximum at 420 nm for PAT ($\epsilon \sim 115$). Ultraviolet–visible spectra were routinely obtained on a Cary Model 14 spectrophotometer. Samples for UV–vis analysis were contained in 1-cm quartz "mini" cells (Precision Cells, Inc.) which were used in conjunction with a pair of black shields, which minimized reflection caused by the 2-mm cell path width. Due to substantial overlap of the PAT absorbance at 420 nm in *tert*-butylbenzene by a product absorbance, the kinetics were followed at 460 nm rather than at the absorbance maximum in this case.

The third method, also utilizing UV–vis spectra for analysis involved the use of Teflon sample cells with solid Teflon plugs and was used for high-pressure experiments. The Teflon tubing ($^1/_8$-in. i.d., $^3/_{16}$-in. o.d.) was cut in 2.5-in. strips which were soaked in ethanol and oven dried. The samples for decomposition were prepared by loading the Teflon tubing with about 0.5 mL of the stock solutions used in method two, closing the tubes with solid Teflon plugs, and sealing the sample tube in three evacuated polyethylene bags, to prevent contamination by the oil bath. The samples were stored in the freezer until use and were run in the same way as those utilizing the ampule technique. This third method, using the Teflon cells, was the only method possible under high pressure; however, it was shown that the three techniques gave identical rates of decomposition of the azo compounds at atmospheric pressure.

Viscosity Determinations. The viscosity of *tert*-butylbenzene was determined via the relationship $\eta/\rho = Bt$ equation using an Oswalt-type viscometer (Kimas size 25). For comparison, viscosities of toluene, ethylbenzene, and cumene were also determined. The standard solvent in this study was benzene at 30° and all viscosities were calculated relative to this solvent.[23] Viscosities were determined in a constant temperature bath controlled to ±0.01 °C by a Sargent thermonitor. η is the absolute viscoisity expressed in centipoise, ρ is the density of the solvent at the temperature at which the viscosity is measured (expressed in g/mL), B is a constant of the apparatus determined during the calibration run with benzene, and t is the time required for the meniscus of the solvent to pass from the upper line to the lower line of the viscometer (flow time). Normally, 5.00 mL of the solvent was pipetted into the viscometer, the viscometer was lowered into the constant temperature bath, and the temperature was allowed to equilibrate for at least 5 min. The solvent was then pulled by suction to bring the meniscus above the upper line, and the flow time was then recorded. This procedure was repeated at least seven times for each solvent at each temperature.

Pressure Experiments. The high-pressure generating equipment and the Teflon sample cells used for all pressure studies have been described in the dissertation of J. V. Behar.[24] High-pressure readings obtained from the bulk modulus cell were calibrated vs. a standard manginin cell.[25]

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Registry No. 1 (X = *p*-NO_2), 16186-97-3; **1** (X = *m*-NO_2), 24760-06-3; **1** (X = H), 981-18-0; **1** (X = *m*-Me), 85354-89-8; **1** (X = *p*-Me), 982-99-0.

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(22) See: Traylor, T. G.; Russell, C. A. *J. Am. Chem. Soc.* **1965**, *87*, 3698.

(23) Rossini, F. D. "Selected Values of Properties of Hydrocarbons and Related Compounds"; API Research Project 44; Carnegie University Press: New York, 1952.

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(25) Ertley, E. W. Ph.D. dissertation, University of California, Riverside, Riverside, CA, 1973.