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RADICAL EFFICIENCY FROM AZO-*p*-CYMENE

W. F. SMITH, JR. and K. L. EDDY
Research Laboratories, Eastman Kodak Company, Rochester, New York 14650, U.S.A.

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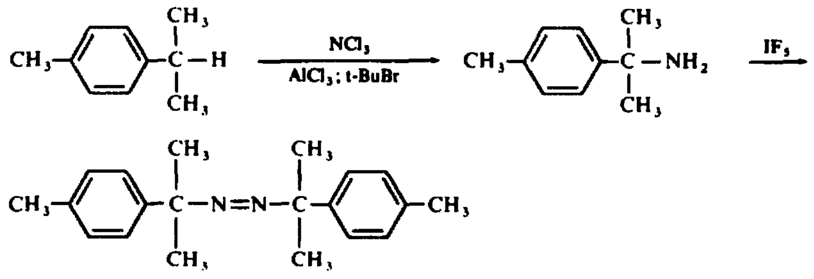
Abstract—The first-order rate constants (k_i) and efficiencies of radical formation (ε) for azo-*p*-cymene were measured in ten solvents spanning 80-fold in absolute viscosity and 30-fold in dielectric constant. Although viscosity plays a major role in the cage effect, specific solvation of *p*-cymyl radicals must also be considered. The k_i exhibit little change with solvent viscosity or dielectric constant, and no trend is apparent. Activation parameters were measured in the most polar solvent (propylene carbonate) and one of the least polar solvents (n-heptadecane). The results indicate either a lack of solvent participation in the thermolysis, or similar solvation of the ground and transition states in both solvents.

AZO-*p*-CYMENE undergoes thermolysis in solution at a rate which is approximately one order of magnitude greater than that of azobisisobutyronitrile at 60°.[1] We find this is a convenient initiation rate for some autoxidation studies which we have undertaken. This paper reports our measurements of the (first-order) rate constants for thermolysis of azo-*p*-cymene at 60° in several solvents, and the efficiency of radical production resulting from these decompositions. Our solvents span a range of approximately 80-fold in absolute viscosity and 30-fold in dielectric constant.

Azo-*p*-cymene was prepared from *p*-cymene by the sequence of reactions:



The synthetic methods have been reported.[2, 3] After four recrystallizations from dichloromethane, the azo compound melted 93·5–94·5° (corr.).

Rate constants (k_i) for decomposition and radical efficiencies (ε) were measured using modifications of existing techniques.[4, 5] Initially formed free *p*-cymyl radicals were scavenged by dissolved oxygen, and the resulting *p*-cymylperoxy radicals were in turn trapped by a phenolic inhibitor. The reaction was followed by observing the *apparent* rate of oxygen consumption (equal to the true rate of oxygen consumption less the rate of N_2 evolution) in a pressure state apparatus similar to that described in the literature.[6] The k_i and ε were measured as follows:

Method A. In solvents where decomposition could be carried to several half-lives in the course of a day, the excess scavenger technique[7, 8] was used. The k_i values were determined from first-order plots of apparent oxygen consumption *vs.* t, the Guggenheim method[9] being used when an infinity reading was not obtained. Efficiencies were calculated from the Equation, $2\varepsilon = 1-(\Delta O_2'/[\mathrm{ACY}]_0)$, where $\Delta O_2'$ is the change in amount of oxygen at t_∞, and $[\mathrm{ACY}]_0$ is the initial concentration of azo-*p*-cymene. If $\varepsilon \cong 0{\cdot}5$, then $\Delta O_2' \cong 0$, and one cannot measure k_i by this method.

Method B. The k_i values were determined from the initial nitrogen evolution rates by dividing the pseudo zero-order rate constants by $[\mathrm{ACY}]_0$. That the reaction was truly first-order was checked by varying $[\mathrm{ACY}]_0$. Efficiencies were then determined in separate runs from the derived Equation,

$$2\varepsilon = 1 - \frac{dO_2'/dt}{k_i[\mathrm{ACY}]_0},$$

where dO_2'/dt is the apparent initial rate of change in the amount of oxygen.

TABLE 1. THERMOLYSIS OF AZO-*p*-CYMENE IN CHLOROBENZENE AT 60·3°

$[\mathrm{ACY}]_0$, $10^2 \times$ M.	p_{O_2}, mm.	Inhibitor	[Inhibitor], M.	k_i sec^{-1} × 10^4	ε
3·84	760	BHT[a]	0·10	2·19	0·75
3·84	745	BHT	0·50	2·09	0·76
1·55	350	BHT	0·50	1·99	0·76
2·88	754	α-$C_{10}H_7OH$	0·25	2·18	0·77
2·88	739	1, 5-$C_{10}H_6(OH)_2$	[b]	2·13	0·78

[a] 2, 6-Di-t-butyl-*p*-cresol.

[b] Saturated solution.

Results for the thermolysis of azo-*p*-cymene in chlorobenzene are given in Table 1. Method A was used for these measurements. The k_i and ε are independent of p_{O_2} (ensuring that all *p*-cymyl radicals are being scavenged by oxygen) and of the concentration and nature of the phenolic inhibitor (ensuring that all *p*-cymylperoxy radicals are being trapped by the hydrogen donors).

TABLE 2. THERMOLYSIS OF AZO-*p*-CYMENE IN SOLVENTS AT 60·3°

Solvent	η[a] cP., 60°	D[b] 25°	ρ_4^{60} g/ml	Method	k_i sec.$^{-1}$ × 10^4	ε
(1) n-Heptane	0·286[10, c]	1·92[10]	0·6492[11, c]	A	1·69	0·73
(2) Toluene	0·380[10]	2·38[10]	0·8295[12]	A	2·22	0·76
(3) Chlorobenzene	0·516[10]	5·62[10]	1·0628[11, c]	A	2·19	0·76
(4) *p*-Cymene	0·524[10]	2·24[10]	0·8253[11, c]	A	1·70	0·70
(5) n-Dodecane	0·805[13]	2·02[10]	0·7210[14]	A	1·64	0·64
(6) Propylene carbonate	1·41[15]	64·6[16]	1·165[17]	B	0·894	0·62
(7) n-Heptadecane	1·79[13]	2·06[10]	0·7519[11, c]	A	1·34	0·56
(8) Hexamethylphosphoric triamide	1·82[18]	29·6[19, 20]	0·994[18]	B	1·15	0·39
(9) Tricresyl phosphate	12·3[d]	6·7[21]	1·136[d]	A	2·28	0·37
(10) Nujol	23·9[d]	—	0·8565[d]	A	1·55	0·30

[a] Numerical superscripts give literature references.

[b] Dielectric constant.

[c] Interpolated value.

[d] This work.

Table 2 summarizes our measurements of k_i and ε at 60·3° in ten solvents. In *all* solvents, the concentration of hydrogen donor was varied to ensure that all peroxy radicals were trapped. In hexamethylposphoric triamide, autoxidation of solvent competed with inhibition by BHT. It was necessary, therefore, to extrapolate a plot of dO_2'/dt *vs.* $[BHT]^{-1}$ in order to obtain the limiting value for dO_2'/dt, i.e., the apparent rate of oxygen consumption at infinite [BHT], where all peroxy radicals are trapped by BHT. The k_i and ε were also shown to be independent of p_{O_2} in tricresyl phosphate and Nujol. Since these were the most viscous solvents, it was assumed that this would hold true in the less viscous solvents as well.

Our results may be summarized as follows:

(1) There is no detectable trend of k_i with solvent viscosity. This result is expected provided azocymene undergoes concerted, two-bond cleavage.[23,27]

(2) The Noyes equation[22] predicts that $k_{diffusion}/k_{cage}$ $(=\varepsilon/1-\varepsilon)$ should be inversely proportional to the viscosity, η and that a limiting ε should be reached at high viscosity. We do not obtain such a dependence (Fig. 1[*]) even among the hydrocarbon solvents. However, k_{diff}/k_{cage} is approximately a monotonic increasing function of η^{-1}, and, therefore, viscosity does play a major role in the cage effect. The fact that k_{diff}/k_{cage} is not proportional to η^{-1} indicates that specific solvation of *p*-cymyl radicals is also important in determining the cage effect. Similar observations have been reported by others for a variety of two-bond initiators.[23, 25, 26, 29]

(3) n-Heptadecane, hexamethylphosphoric triamide, and propylene carbonate have similar viscosities but widely different dielectric constants. The effect of solvent polarity on ε is unpredictable, thus underlining the importance of specific solvent-radical interactions. On the other hand, the first-order rate constants (k_i) diminish slightly with increasing dielectric constant. This effect contrasts with azocumene where Nelsen and Bartlett[23] found an approximately 30% increase in k_i in 3·9M thiophenol-benzene compared to n-dodecane.

Table 3 gives k_i values for thermolysis of azo-*p*-cymene at three temperatures in n-heptadecane (D = 2·06) and propylene carbonate (D = 64·6). An Eyring plot of these data gives, after least squares treatment: in n-heptadecane, $\Delta H^\ddagger = 30{\cdot}2$ kcal/mole, $\Delta S^\ddagger = 14{\cdot}3$ e.u.; in propylene carbonate, $\Delta H^\ddagger = 30{\cdot}4$ kcal/mole, $\Delta S^\ddagger = 14{\cdot}5$ e.u. $\Delta H^\ddagger$

TABLE 3. TEMPERATURE DEPENDENCE OF FIRST-ORDER RATE CONSTANT FOR DECOMPOSITION OF AZO-*p*-CYMENE.

Solvent	*t*, °C.	k_i, sec.$^{-1}$ × 10^4
n-$C_{17}H_{36}$	49·9	0·374
	60·3	1·34
	70·2	5·41
Propylene carbonate	49·9	0·281
	60·3	0·894
	70·2	4·64

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[*] The use of kinematic, rather than absolute, viscosity derives from a suggestion of Nelson and Bartlett[23] that k_{diff} may be proportional to the self-diffusion coefficient of the solvent, which in turn is proportional to ρ/ absolute viscosity.[24]

and $\Delta S^{\ddagger}$ are nearly constant despite a 30-fold change in solvent dielectric constant. If charge reorganization were significant in the transition state of this reaction, one would expect this to be reflected in a solvent effect on $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$. That such a solvent effect is not observed is then evidence either for a lack of solvent participation in the cleavage reaction, or for similar solvation of the ground and transition states in both solvents. The first-order rate constant for thermolysis of phenylazotriphenylmethane (PAT) is also insensitive to the dielectric constant of the solvent.[28] In this case the effect has been shown to be a result of compensating values of $\Delta\Delta H^{\ddagger}$ and $\Delta\Delta S^{\ddagger}$ which are of an order of magnitude greater than those observed with azo-*p*-cymene. This difference is undoubtedly due to the unsymmetrical structure of PAT, which may result in its being a one-bond initiator.[27]

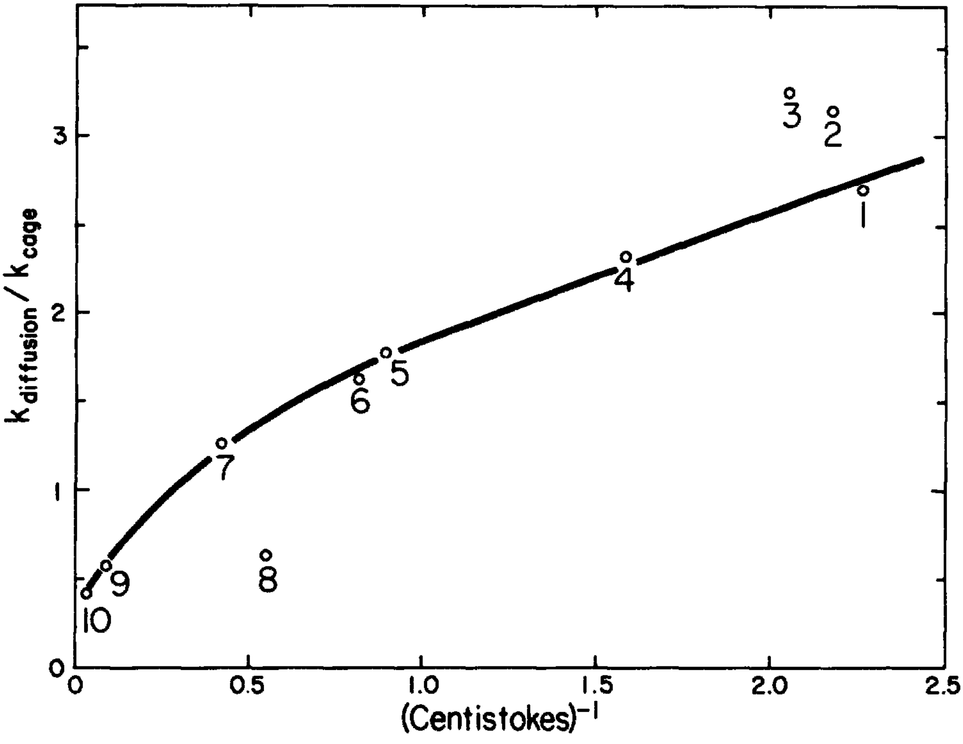

FIG. 1. Effect of solvent viscosity on the ratio of rate constants for diffusion *vs.* combination and disproportionation of caged *p*-cymyl radicals.

(4) The efficiencies of radical production from azo-*p*-cymene and azocumene are nearly identical in toluene and n-dodecane.[23] In addition, ε for azocumene in solvent cumene $\cong$ ε for azo-*p*-cymene in *p*-cymene. However, in chlorobenzene the efficiencies differ,* and $(k_{\rm diff}/k_{\rm cage})_{\text{azo-}p\text{-cymene}} = 1{\cdot}4\ (k_{\rm diff}/k_{\rm cage})_{\rm azocumene}$. The reasons for this are not known, since a substituent effect on $k_{\rm diff}$ and/or $k_{\rm cage}$ should manifest itself in more than one solvent.

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* Using Method B, we find that for azocumene in chlorobenzene $k_i = 1{\cdot}27 \times 10^{-4}$ sec^{-1} and $\varepsilon = 0{\cdot}70$, independent of p_{O_2} and [BHT]. Nelson and Bartlett[23] have reported $\varepsilon \cong 0{\cdot}60$ for azocumene in chlorobenzene.

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