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Solvent Effects in the Oxidation of Hydrocarbons. II. Oxidations of Tetralin in Various Solvents

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The rates of oxidation of 1.47M tetralin in a variety of solvents at 70°C in the presence of 1.00×10^{-2}M AIBN varied by a factor of 2.9, ranging from 6.39×10^{-6} mol/*l*/sec in *n*-decane to 1.84×10^{-5} mol/*l*/sec in nitromethane. The rate of oxidation was dependent on the composition of the solution as well as the kinds of solvents. It was found that the solvents affected the initiation step approximately as much as they affected the propagation and/or temination step. The rate of initiation by AIBN was mainly dependent on the viscosity of the medium, while that of propagation and termination was mainly determined by the dielectric constant of the medium. The correlation between $\log (k_p/(2k_t)^{1/2})$ and $(D-1)/(2D+1)$ was discussed, where k_p and k_t are the rate constants for propagation and termination steps, respectively, and D is the dielectric constant of the medium, under conditions where the complication caused by the selective solvation could be excluded.

Although it was once accepted that the solvent effects in the reactions of free radicals and atoms are small in contrast to the ionic reactions, it is known nowadays that the solvent affects both the rate and the course of the free radical reactions.[1,2] The solvent effects in the autoxidation of hydrocarbons, a typical example of the reaction by a free radical mechanism, have been studied by several investigators. Zaikov[3-6] studied the oxidation of methyl ethyl ketone in benzene and acetic acid solutions by varying the compositions of the reactant and the solvents, and found that the rates of oxidation and the rate constants could be well correlated with Kirkwood equation[7]

$$\log(\text{rate or rate constant}) = a(D-1)/(2D+1)+b \quad (1)$$

where D is the dielectric constant of the medium, and a and b are constants. Hendry and Russell,[8] and Howard and Ingold[9] studied the oxidation of several hydrocarbons in a number of solvents and found that the rates of oxidation increased with the increase in the dielectric constants of the solvents. They suggested that the dipolar transition state was involved in the propagation step and the contribution of the solvation at this stage enhanced the rates of propagation and oxidation. They also suggested that the solvation is greater at the ground state than at the transition state in the termination step, which decreased the rate of termination and increased the rate of oxidation.[8]

Since then, several papers concerning the solvent effects on the autoxidation of hydrocarbons have been presented and the correlation between the rates of oxidation and the dielectric function, $(D-1)/(2D+1)$, has been discussed.[10-12]

However, two important problems have been overlooked. One is the variation of the dielectric constant with temperature and the other is the difference between the bulk dielectric constant and the microscopic dielectric constant. In particular, the microscopic dielectric constant in the immediate vicinity of a reactant particle and the existence, extent, and nature of selective solvation have received little attention. This paper deals with the study on the solvent effects in the oxidation of tetralin taking the problems mentioned above into consideration. Tetralin was chosen as the oxidant since its oxidation mechanism is now well established,

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[1] G. A. Russell, *J. Am. Chem. Soc.*, **79**, 2977 (1957), and the subsequent papers.

[2] E. S. Huyser, "Advances in Free-Radical Chemistry," Vol. I, ed. by G. H. Williams, Logos Press, London (1965), Chap. 3.

[3] G. E. Zaikov, *Neftekhimiya*, **3**, 381 (1963).

[4] G. E. Zaikov and Z. K. Maizus, *Dokl. Akad. Nauk SSSR*, **150**, 116 (1963).

[5] G. E. Zaikov and Z. K. Maizus, Advances in Chemistry Series, **75**, Am. Chem. Soc., Washington D. C. (1968), p. 150.

[6] G. E. Zaikov, *Kinetika i Kataliz*, **9**, 511 (1968).

[7] J. G. Kirkwood, *J. Chem. Phys.*, **2**, 351 (1934).

[8] D. G. Hendry and G. A. Russell, *J. Am. Chem. Soc.*, **86**, 2368 (1964).

[9] J. A. Howard and K. U. Ingold, *Can. J. Chem.*, **42**, 1044, 1250 (1964); **44**, 1119 (1966).

[10] Y. Kamiya, This Bulletin, **38**, 2156 (1965).

[11] J. Yamashita, O. Yamamoto, K. Shimizu and H. Hashimoto, *Kogyo Kagaku Zasshi (J. Chem. Soc. Japan, Ind. Chem. Sect.)*, **71**, 225 (1968).

[12] H. Masuda, K. Kobayashi and N. Ohta, *ibid.*, **71**, 994 (1968).

and in addition its oxidation rate is greater than those of other hydrocarbons. This is advantageous for studying the oxidation of dilute solutions.

Results and Discussion

The autoxidation of tetralin in a variety of solvents at 70°C initiated by azobisisobutyronitrile (AIBN) were carried out in order to estimate the solvent effects on the rates of oxidation. The results are summarized in Table 1. The observed rates of oxygen absorption were corrected for nitrogen evolved from AIBN and for oxygen absorbed and evolved in the initiation and termination steps respectively, the correction factor being $R_i(1/e-1)/2$ where R_i is the rate of initiation and e is the efficiency of AIBN for radical production.[13] Table 1 indicates that the rates of oxidation of 1.47M tetralin in 35 solvents studied differ by a factor of 2.9, ranging from 6.39×10^{-6} mol/*l*/sec in *n*-decane to 1.84×10^{-5} mol/*l*/sec in nitromethane.

TABLE 1. RATES OF OXIDATION OF TETRALIN IN VARIOUS SOLVENTS 70°C
[AIBN]$=1.00\times10^{-2}$M, [tetralin]$=1.47$M

No.	Solvent	$-dO_2/dt$, mol/*l*/sec
	(i) Aromatic hydrocarbon	
1	*t*-Butylbenzene	0.779×10^{-5}
2	*m*-Dichlorobenzene	0.946
3	Bromobenzene	0.999
4	1-Chloronaphthalene	1.00
5	Chlorobenzene	1.05
6	Nitrobenzene	1.34
	(ii) Alphatic hydrocarbon	
7	*n*-Decane	0.639
8	*n*-Nonane	0.662
9	*n*-Octane	0.666
10	Tetrachloroethylene	0.743
11	2-Nitropropane	1.36
12	1-Nitropropane	1.42
13	Nitroethane	1.54
14	Nitromethane	1.84
	(iii) Fatty acid	
15	Isovaleric acid	0.798
16	Valeric acid	0.814
17	Butyric acid	0.909
18	Acetic acid	1.21
	(iv) Alcohol	
19	1-Propanol	0.671
20	1-Pentanol	0.704
21	1-Octanol	0.790
	(v) Ketone	
22	Acetophenone	0.998
	(vi) Ether	
23	Anisole	1.04
	(vii) Ester	
24	Butyl stearate	0.664
25	Dibutyl sebacate	0.729
26	Dibutyl phthalate	0.875
27	Amyl acetate	0.878
28	Diethyl maleate	0.996
29	Ethyl cinnamate	1.00
30	Butyl acetate	1.01
31	Ethyl benzoate	1.04
32	Methyl benzoate	1.04
33	Ethyl propionate	1.06
34	Propyl acetate	1.07
35	Diethyl malonate	1.12

The rates of oxidation are dependent on the composition of the solutions as well. The effects of dilution on the rates of oxidation of tetralin in eight inert solvents, *n*-decane, butyl stearate, butyric acid, anisole, chlorobenzene, diethyl maleate, acetophenone and nitrobenzene, are summarized in Table 2. The rate of oxidation of tetralin is given by the following equation:

$$-dO_2/dt = k_p(2k_t)^{-1/2}[\mathrm{RH}]R_i^{1/2}$$
$$= k_p(ek_i/k_t)^{1/2}[\mathrm{RH}][\mathrm{AIBN}]^{1/2} \qquad (2)$$

where k_i is the rate constant for the unimolecular decomposition of AIBN, and k_p and k_t are the rate constants for the following propagation and termination steps respectively.

TABLE 2. EFFECTS OF DILUTION IN THE OXIDATION OF TETRLIN IN VARIOUS SOLVENTS[a)]
70°C, [AIBN]$=1.00\times10^{-2}$M

Tetralin, M	6.61	5.88	4.41	2.94	1.47	0.668
Solvent		$-dO_2/dt\times10^5$, mol/*l*/sec				
n-Decane		2.98	2.11	1.35	0.639	0.297
Butyl stearate		3.01	2.08	1.27	0.664	0.295
Butyric acid		3.32	2.60	1.77	0.909	0.404
Anisole		3.48	2.79	1.98	1.04	0.494
Chloro-benzene	3.91	3.55	2.84	1.95	1.05	0.486
Diethyl maleate		3.51	2.81	1.91	0.996	0.494
Acetophenone		3.58	2.93	1.99	1.01	0.464
Nitrobenzene	4.16	4.02	3.19	2.45	1.34	0.614

a) The rate of oxidation of pure tetralin under the same reaction conditions was 3.95×10^{-5} mol/*l*/sec.

$$\mathrm{RO_2\cdot} + \mathrm{RH} \xrightarrow{k_p} \mathrm{ROOH} + \mathrm{R\cdot}$$

$$\mathrm{RO_2\cdot} + \mathrm{RO_2\cdot} \xrightarrow{k_t} \text{tetralone} + \text{tetralol} + \mathrm{O_2}$$

Equation (2) implys that the rate of oxidation of tetralin is strictly first with respect to tetralin concentration at a constant initiator concentration. However, plots of the rates of oxidation in Table 2 as a function of tetralin concentration always show some curvature and, as shown in Fig. 1, the values of $k_p(ek_i/k_t)^{1/2}$ calculated from Eq. (2) varies monotonously with the tetralin concentration.

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13) E. Niki, M. Kuwata, Y. Kamiya and N. Ohta, *ibid.*, **70**, 1679 (1967).

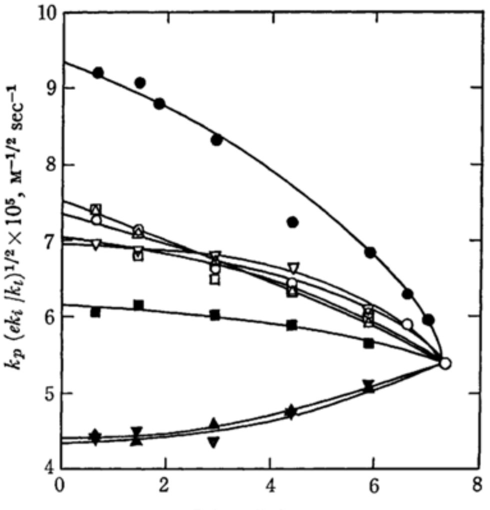

Fig. 1. Plots of $k_p\,(ek_i/k_t)^{1/2}$ as a function of tetralin concentration.
70°C, [AIBN] = 1.00×10^{-2}M

▲	*n*-Decane	▼	Butyl stearate
■	Butyric acid	△	Anisole
○	Chlorobenzene	□	Diethyl maleate
▽	Acetophenone	●	Nitrobenzene

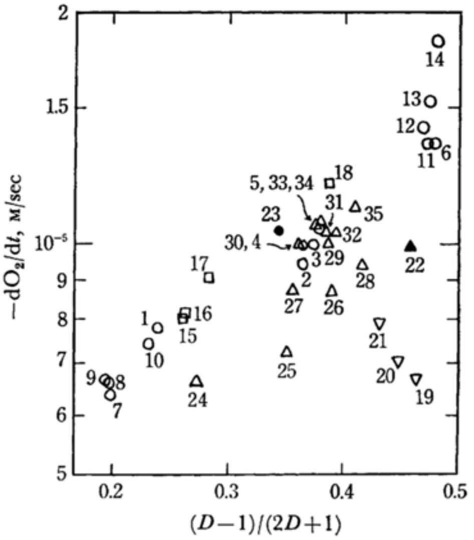

Fig. 3. Plots of the rates of oxidations of tetralin in various solvents as a function of dielectric function.
70°C, [AIBN] = 1.00×10^{-2}M, [tetralin] = 1.47M

○	Hydrocarbon	▲	Ketone
□	Acid	●	Ether
▽	Alcohol	△	Ester

That the rates of oxidation of tetralin are dependent on the nature of the solvents is more clearly established by oxidation in the binary inert solvents media. The rates of oxidation of tetralin in the binary solvents are shown in Fig. 2. A deviation from linearity is again observed for each system, and it is interesting that the curves in nitrobenzene - *n*-decane and nitrobenzene - chlorobenzene systems are convex upward, while that in nitrobenzene-acetophenone system convex downward.

Data in literature and in this work indicate that the rate of oxidation of hydrocarbon increases, as a whole, with the increase in the dielectric constant of the medium. However, with regard to the correlation between the rate of oxidation and the dielectric function, $(D-1)/(2D+1)$, some are satisfactory but others are not. In Fig. 3 are shown the plots of the rates of oxidation of tetralin in Table 1 against the dielectric function of the solvents. Fugure 3 shows that the solvents evidently affect the rates of oxidation but the correlation predicted from Eq. (1) is not applicable.

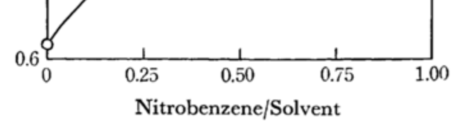

Fig. 2. Rates of oxidation of tetralin in binary solvents.
70°C, [AIBN] = 1.00×10^{-2}M, [tetralin] = 1.47M

○	Nitrobenzene + *n*-decane
□	Nitrobenzene + chlorobenzene
△	Nitrobenzene + acetophenone

As shown in Eq. (2), the rate of oxidation is determined by k_p, k_t, e, and k_i at constant concentration of hydrocarbon and initiator. The solvent may affect some or, more probably, all of the above mentioned four constants. The kinetic data for the oxidation of 1.47M tetralin in the various solvents are summarized in Table 3 together with the physical properties of the media measured at 70°C.14,15) As shown in Table 3, the values of $k_p(ek_i/k_t)^{1/2}$, $(ek_i)^{1/2}$, and $k_p/(2k_t)^{1/2}$ range from 4.35×10^{-5} to 9.12×10^{-5} $l^{1/2}$/mol$^{1/2}$/sec (by a factor of 2.1), from 3.46×10^{-3} to 5.31×10^{-3} sec$^{-1/2}$ (by a factor of 1.5), and from 7.73×10^{-3} to 1.23×10^{-2} (l/mol/sec)$^{1/2}$ (by a factor of 1.6), respectively. Thus, in the oxidation of tetralin initiated by AIBN, the solvents give an effect about as much in the initiation step as in the propagation and/or termination step. As discussed in the preceding paper,15) the

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14) E. Niki, Y. Kamiya and N. Ohta, This Bulletin, in contribution.

15) E. Niki, Y. Kamiya and N. Ohta, *ibid.*, in contribution.

TABLE 3. OXIDATION OF 1.47M TETRALIN IN VARIOUS SOLVENTS AT 70°C, [AIBN]=1.00×10⁻²M

Solvent	D[b]	$\frac{(D-1)}{(2D+1)}$	η[c] centi-poise	d[d]	M[e]	$-dO_2/dt$ $\times 10^5$ M/sec	$k_p(ek_i/k_t)^{1/2}$ $\times 10^5$ $M^{-1/2}sec^{-1}$	k_i $\times 10^5$ sec^{-1}	e	ek_i $\times 10^5$ sec^{-1}	$(ek_i)^{1/2}$ $\times 10^3$ $sec^{-1/2}$	$k_p/(2k_t)^{1/2}$ $\times 10^3$ $(M\,sec)^{-1/2}$
n-Decane	2.069	0.208	0.5633	0.6921	142.3	0.639	4.35	3.05	0.518	1.58	3.98	7.73
Tetralin[a]	2.657	0.260	0.9869	0.9302	132.2	3.95	5.38	4.22	0.483	2.04	4.52	8.44
Butyl stearate	2.857	0.277	2.337	0.8189	340.6	0.664	4.52	3.67	0.327	1.20	3.46	9.29
Butyric acid	2.937	0.282	0.8232	0.9083	88.1	0.909	6.18	3.64	0.563	2.05	4.53	9.65
Anisole	3.651	0.319	0.6232	0.9470	108.1	1.04	7.07	3.89	0.656	2.55	5.05	9.93
Chlorobenzene	4.440	0.348	0.5568	1.0523	112.6	1.05	7.14	4.10	0.688	2.82	5.31	9.50
Diethyl maleate	5.811	0.381	1.211	1.0187	172.2	0.996	6.78	3.64	0.489	1.78	4.22	11.4
Acetophenone	11.21	0.436	0.8958	0.9853	120.1	1.01	6.87	4.41	0.569	2.51	5.01	9.72
Nitrobenzene	21.10	0.465	0.9694	1.1538	123.1	1.34	9.12	4.70	0.581	2.73	5.23	12.3

a) Pure tetralin.
b) Dielectric constant of the solution containing 20 vol% tetralin and 80 vol% solvent measured at 70°C.[14]
c) Viscosity of the solution measured at 70°C.[15]
d) Density of the pure solvent at 70°C.
e) Molecular weight of the solvent.

value of k_i was larger in the aromatic solvent than in the aliphatic solvent and that of e was dependent more on the viscosity of the solution rather than its polarity. But the solvent affected e more than k_i and the rate of initiation by AIBN was mainly dependent on the viscosity of the medium.

Before discussing the correlation between log-$(k_p/((2k_t)^{1/2})$ and $(D-1)/(2D+1)$, the error involved in the measurement should be examined. The rates of oxidation of tetralin in various solvents were fairly good in reproducibility. The largest negative and positive deviations from the lines in Fig. 1 are those for the oxidation of 4.41M tetralin in nitrobenzene and 0.668M tetralin in diethyl maleate, the deviations being about 6%. It may be said that the experimental error involved in most of the measurements is within 5%. On the other hand, the values of e and k_i were reproducible within an experimental error of 5%. The physical constants determined for the media may be more accurate. Thus we could say that the results obtained in this work are accurate within an experimental error of 5% and 10% for the worst.

Now we should like to discuss the correlation between $k_p/k_t^{1/2}$ and the dielectric function. If the solvent effects on the propagation and termination[16] steps may be attributed to the solvation of the solvents at the transition state and/or ground state as proposed by Hendry and Russell,[8] and Howard and Ingold,[9] and if both k_p and k_t are expressed in terms of the dielectric function, $(D-1)/(2D+1)$, as in Eq. (1), then logarithm of $k_p/k_t^{1/2}$ should be proportional to $(D-1)/(2D+1)$. In the meantime, tetralin acts not only as a reactant but also as a solvent. The solution has been regarded as a medium of uniform dielectric constant. However, this assumption is not valid when one of the solvents solvates more preferentially than the others. Such a preferential, or selective, solvation has been observed in some cases.[18] In this case, the bulk dielectric constant of the medium is not important, but the microscopic dielectric constant in the immediate vicinity of a reactant particle may be the more important factor in determining the extent of solvation. Although the bulk dielectric constant can be measured, the microscopic dielectric constant can not be measured easily, and the extent of the selective solvation is hard to evaluate from the

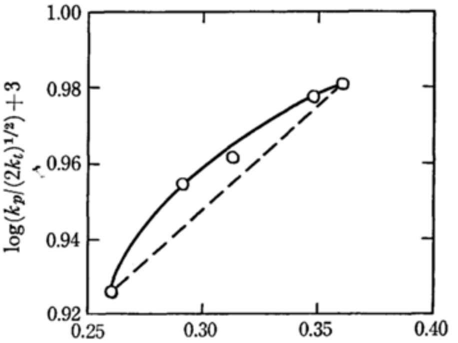

Fig. 4. Plots of $\log(k_p/(2k_t)^{1/2})$in the oxidation of tetralin in chlorobenzene against the dielectric function, 70°C.

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[16] It is known that the viscosity of the medium has significant effect on the bimolecular interaction of the tertiary peroxy radicals.[17] However, the bimolecular interaction of the tetralylperoxy radicals at 70°C may be all terminating and no free tetraloxy radical should be produced. Therefore, the viscosity of the solution may have little effect on the termination step in the oxidation of tetralin.

[17] R. Hiatt and T. G. Traylor, *J. Am. Chem. Soc.*, **87**, 3766 (1965).

[18] N. Tokura, *Yukigosei Kagaku Kyokaishi (J. Soc. Org. Synth. Chem. Japan)*, **25**, 1084 (1967).

conventional kinetic study. If the selective solvation does exist, then the plot of $\log(k_p/(2k_t)^{1/2})$ as a function of $(D-1)/(2D+1)$ should give a curve convex upward. In Fig. 4 is shown the plot of $\log(k_p/(2k_t)^{1/2})$ in the oxidation of tetralin in chlorobenzene, calculated from $k_p(ek_t/k_t)^{1/2}$ and ek_t measured for each mixture,[15] against the dielectric function calculated from the measured dielectric constants of the media at 70°C.[14] The curve is indeed convex upward, but the curvature is small and it is difficult to measure the extent of selective solvation. Although the problem of selective solvation is interesting and important itself, it complicates the situation and it is desirable to disregard the problem discussing the correlation between the rate constant and the dielectric function. One possible approach so as to reduce the effect of selective solvation may be the oxidation of the very dilute reactant in a large excess of solvent. However, the lower the concentration, the smaller the rate of oxidation and the shorter the kinetic chain length, and the radical produced from the initiator may also participate in the terminating reactions, complicating the over-all kinetics.[19] The most suitable method may be the extrapolation to the infinite dilution of the reactant by the solvent. In Fig. 5 is shown the plot of $\log(k_p/(2k_t)^{1/2})$, calculated from $k_p(ek_t/k_t)^{1/2}$ and ek_t extrapolated to the infinite dilution, against the dielectric function of the neat solvent at 70°C. A fairly good linear correlation between the two functions is observed, although $\log(k_p/(2k_t)^{1/2})$ for the aromatic solvents, especially for acetophenone, is somewhat smaller than expected.

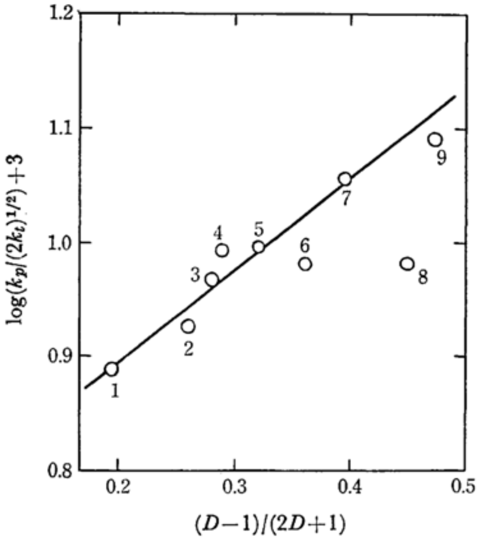

Fig. 5. Plots of $\log(k_p/(2k_t)^{1/2})$ at the infinite dilution as a function of the dielectric function.

1: *n*-Decane
2: Tetralin
3: Butyl stearate
4: Butyric acid
5: Anisole
6: Chlorobenzene
7: Diethyl maleate
8: Acetophenone
9: Nitrobenzene

Powling and Bernstein[20] introduced the function of $d(D-1)/M(2D+1)$, where d and M are density and molecular weight of the solvent respectively, on the study of the heats of tautomerization of several substances in a variety of solvents on the assumption that the radii of the reactants and the transition state are dependent on the molar volume of the solvent. The plot of $\log(k_p/(2k_t)^{1/2})$ at the infinite dilution against $d(D-1)/M(2D+1)$, however, gave a poorer correlation than that against $(D-1)/(2D+1)$.

In addition to the general dielectric effect some specific interactions between the solute and the solvent such as hydrogen bonding, π-complex and charge transfer complex formations may also participate, to some extent, in the solvent effects. It has been known that the peroxy radical forms hydrogen bonding with the hydroxy group such as water, acid and alcohol. Hendry and Russell[8] observed that the rates of oxidation of cyclohexene and cumene in acetic acid were smaller than anticipated, and they interpreted this as being due to the decrease in the reactivity of the hydrogen-bonded peroxy radical. In the present study, however, the rates of oxidation of tetralin in fatty acids were not small. This might be because although such a hydrogen bonding, if any, would decrease the rate of propagation, it would also decrease the rate of termination. Such a phenomenon was observed experimentally by Zaikov.[5] The formation of π-complex was observed for chlorine atom and alkoxy radical,[1] but this π-complexing may not be so important for the peroxy radical since the electron affinity of the peroxy radical may be smaller than chlorine atom and alkoxy radical.[21] In any event, if the peroxy radical forms complex with the solvent and desolvation is necessary for both propagation and termination steps, both k_p and k_t values are expected to decrease and the effect of complex formation on the over-all rate or on $k_p/(2k_t)^{1/2}$ may in part be cancelled.

In summary, in the oxidation of tetralin initiated

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19) C. Gadelle and G. Clement, *Bull. Soc. Chim. France*, **1967**, 1175.

20) J. Powling and H. J. Bernstein, *J. Am. Chem. Soc.*, **73**, 1815, 4353 (1951).

21) The speculation that the π-complex formation between the tetralylperoxy radical and the aromatic solvents should give smaller values for $k_p/(2k_t)^{1/2}$ than expected in Fig. 5 may be ruled out. Because, if so, the decrease should be in the order, anisole>chlorobenzene>nitrobenzene>acetophenone, as predicted by the electron density at the aromatic ring. However, this is not the case as is clear from Fig. 5. This does not necessarily deny the π-complex formation of the peroxy radical, and the information on this complex formation may be obtained by studying the products distribution in the various solvents.

by AIBN the solvents affect approximately as much the initiation step as the propagation and/or termination step. The effects of solvents on the initiation step are mainly determined by the viscosity of the medium, while those on the propagation and/or termination step are mainly dependent on the dielectric constant of the medium.

Experimental

Materials used were the same as in the preceding papers.[14,15] All of the solvents were found to be oxidation resistant under the experimental conditions employed here. Oxidation was performed under atmospheric pressure of oxygen and the oxygen uptake was measured periodically in a constant pressure closed system. Satisfactory and reproducible straight line was obtained.