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Decay Reactions of Aryldiazenyl Radicals in Solution

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The decay processes of aryldiazenyl radicals were studied by using a time-resolved ESR method. The first order rate constants of decomposition were determined at −117—−48 °C in cyclopropane solutions in the presence or absence of olefins. Aryldiazenyl radicals were relatively persistent and the k_1 of phenyldiazenyl-d_5 at −96 °C in cyclopropane was 34 s^{-1}. The k_1 of 20 aryldiazenyl radicals at −96 °C afforded a ρ value of +1.53 (r=0.91) in a Hammett plot. Activation energies ranged from 46.2 to 25.2 kJ mol^{-1} and the frequency factors, log A, from 13.2 to 8.2 s^{-1}. The second-order decay rates were measured at the initial period of the decay process at lower temperatures, in a batch system (cyclopropane) and in a flow system (isohexane). The rate constant of phenyldiazenyl-d_5 in cyclopropane was $9.2 \cdot 10^5$ M^{-1} s^{-1} at −93 °C and the Arrhenius parameters were E_a=23.5 kJ mol^{-1} and log A=12.77 M^{-1} s^{-1}, respectively.

Aryldiazenyl radicals have been studied as transient radicals in organic syntheses such as the Gomberg-Bachmann reaction,[1] and from theoretical interests in thermolysis of acylarylnitrosamines[2] and of aryl(triphenylmethyl)diazenes.[3] Informations concerning the lifetime of the radicals were reported in a trapping experiment of the radicals by using triphenylmethyl radicals[4] and in CIDNP experiment using diazenes or nitrosamine.[4—6] These investigations suggested a very rapid decay nature of aryldiazenyl radicals. Another estimation of a rather slow decay rate of phenyldiazenyl radicals was reported from a study of activation free energy of azo compounds.[7] We could observe aryldiazenyl radicals in solutions by an ESR technique and this fact supported a rather persistent nature of the radicals.[8] We will here report the rate constants of decomposition of aryldiazenyl radicals in solutions, obtained in a time-resolved ESR study.

Experimental

(1) Time-Resolved ESR Spectroscopy a) Apparatus. The measurement of the decay rates of aryldiazenyl radicals was carried out on a Varian E-109E spectrometer with 100 kHz modulation for the first order decay rate, after insertion of a 100 kOhm resistance in the receiver to attain a faster responce of about 0.3 ms. For determination of second order rate constant, we constructed a 1 MHz modulation amplifier and a coherent receiver by the method of Smith and coworkers,[9] thereby a pair of hair-pin type modulation coil was set around the Dewar tube in the cavity.

To follow the decay of aryldiazenyl radicals, we measured one line of the ESR spectrum of aryldiazenyl radical at a specified resonance magnetic field under a rather high modulation amplitude. The signal intensities were transferred via a transient memory, Biomation 805, into a microcomputer, Multi-16, accumulating up to 2^{16} transients. The microcomputer output decay curves, signal intensity-time plots for the first and second order rate analyses, and the calculated rate constants.

For flash photolysis we used a 1 kW Xe lamp with a rotating sector (flash duration 30 to 50 ms) for k_1 measurements and a Nitrogen Laser, Molectron UV-14 for k_2 measurements. The block diagram of the system was shown in Fig. 1.

b) Reaction Cell. For determination of k_1 and k_2 using a higher concentration of aryl(arylthio)diazenes, $\geqslant 2 \cdot 10^{-2}$ M[††], we used a sample tube as that used in a previous study.[8] (We call this a batch method.) For measurements of k_2 using a solution of low concentration, $4 \cdot 10^{-4}$ M, we adopted a flow method, using a sample tube (quartz, ϕ 4 mm), closed by a screw cap, through which a concentric inlet tube (Pyrex, ϕ 2 mm), a teflon outlet tube (ϕ 2 mm), and a copper-constantan thermocouple were introduced.

In the flow system an air-free sample solution under Ar, 300—500 ml, cooled in Dry Ice-methanol bath, was forced to flow into the sample tube by Ar pressure, via a cold thermostat (ca. −130 °C) and a cold path (teflon, ca. −100 °C),

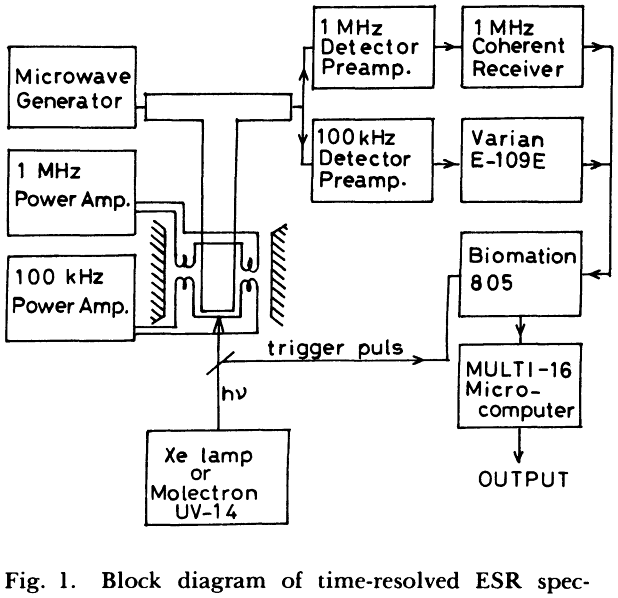

Fig. 1. Block diagram of time-resolved ESR spectrometer.

[††] 1 M=1 mol dm^{-3}.

both regulated by cold nitrogen tream and monitored by copper-constantan thermocouple. About 10 m teflon tube in the thermostat was sufficient to attain a desired low temperature. The sample tube was placed in the Dewar tube in the ESR cavity. (Ref. Fig. 6 and the description on it.)

(2) Materials. a) Aryl(arylthio)diazenes. Aryl(arylthio)diazenes were prepared as described in a previous paper.[8] Additional diazenes used in this kinetic study were listed in Table 1.

For the measurement of second order rate constants we used perdeuteriophenyl-, 4-methoxy-3,5-dideuteriophenyl-, and 4-chloro-3,5-dideuteriophenyldiazenyl radicals to eliminate the hfs of ESR spectrum due to 3,5-hydrogens. The preparation of 4-substituted 3,5-dideuterioanilines was performed as follows: 1) 4-nitrophenol was deuterated by heating with D_2O–D_2SO_4, then methylated by diazomethane and then reduced by $SnCl_2$–HCl, ii) 4-nitroaniline was deutetrated by heating with D_2O–DCl, and then transformed into 4-chloro-3,5-dideuterionitrobenzene by the Sandmeyer reaction and then reduced to aniline. The deuterium exchange was monitored by ^{1}H NMR method.

b) Solvents. Cyclopropane, methylcyclopentane, toluene, 1-butene, *cis*-2-butene, ethoxyethene, propene, bromoethene, 1-chloropropene, were used after they have been degassed by repeated freeze and thaw in vacuum and distilled from bulb into sample tube. Isohexane for the flow method was purified by wasing with concd. H_2SO_4, boiled over sodium wire, followed by distillation over lithium tetrahydridoaluminate under Ar. The purity of isohexane was monitored by determining peroxyl radical during photolysis by ESR measurement.

(3) Kinetic Analysis. a) First Order Reaction Rate. Decay curves obtained by using time-resolved ESR technique were examined by plotting, 1) $1/(R\cdot)_t$ against time for second order decay reaction, and 2) $\ln[(R\cdot)_0/(R\cdot)_t]$ against time for first order reaction, here $(R\cdot)_0$ and $(R\cdot)_t$ stand for the concentrations of aryldiazenyl radicals at time 0 and t, respectively (Figs. 2 and 3).

b) Second Order Reaction Rate. In a batch method we

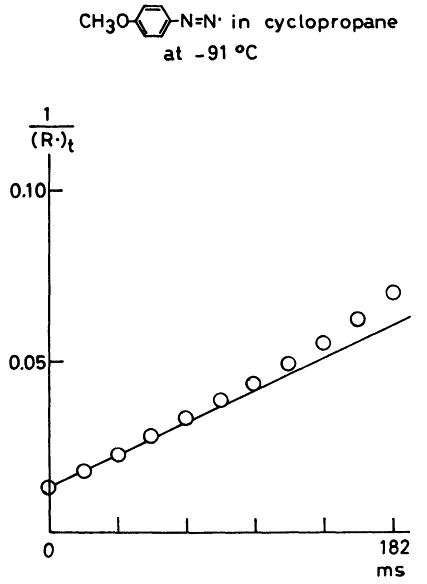

Fig. 2. Polt of $1/(R\cdot)_t$ against time.

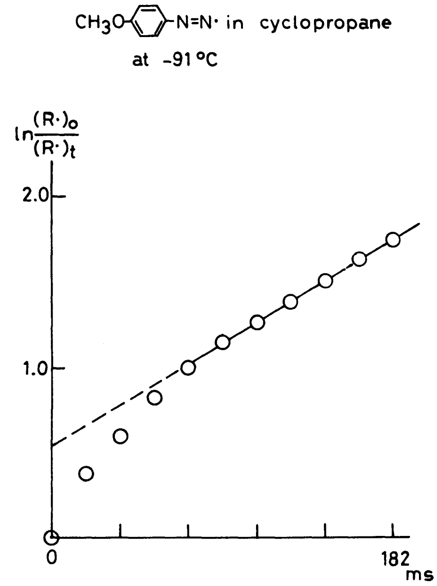

Fig. 3. Plot of ln $[(R\cdot)_0/(R\cdot)_t]$ against time.

Table 1. Aryl(4-*t*-butylphenylthio)diazenes

Subst. in Aryl	Mp (θ_m/°C)	ESR spectra					Remarks elemental		anal.
		g-Value	Hfs. constant						
			a_N1	a_N2	$a_{3,5\text{-H}}$	*n*-H	C/%	H/%	N/%
3-CN	60—62, d	2.0003	9.30	23.7	1.00	1H	f. 68.91 c. 69.12 for $C_{17}H_{17}N_3S$	5.83 5.80	14.13 14.22
4-CN	83.5—84·5, d	2.0004	9.42	23.6	1.10	2H	f. 69.15	5.79	14.12
3-CH_3CO	66.3—69.2, d	2.0004	9.35	24.5	1.10	1H	f. 69.39 c. 69.20 for $C_{18}H_{20}N_2OS$	6.60 6.45	9.39 8.97
4-CH_3CO	61—63, d	2.0003	9.50	22.9	1.15	2H	f. 68.94	6.66	9.18
4-CH_3O-3,5-*d*$_2$	61—62, d	2.0004	9.25	22.3	none	0	3,5-d%: 90% in 4-CH_3O-3,5-d_2-$C_6H_2NO_2$		
4-Cl-3,5-*d*$_2$	29—31, d	2.0004	9.35	23.2	0.50 $a_{2\text{-H}}$?	1H?	3,5-d%: 92% in 4-Cl-3,5-d_2-$C_6H_2NH_2$		

used solutions of aryl(arylthio)diazenes of a higher concentration, $2.0\cdot10^{-2}$ M. In this case the light introduced in the solution was completely absorbed and the radicals formed in the solution were not distributed homogenously in the solution but the radical concentration decreased exponentially from the front surface of the sample tube into the inner part of solution. On this problem H. Fischer and his coworkers have discussed and estimated the accuracy of the experimental values of k_2.[10] We have analyzed the decay curves by taking account of this exponential distribution of the radicals in the following way.

In our experiments we assumed a front area of the light path to be half of the surface of the sample tube of inner diameter 0.253 cm, multiplied by 1.20 cm height, and devided by 2 because of the lattice of the cavity window.

The distibution of aryldiazenyl radicals in solution at time 0 was assumed to be the exponential curve A as depicted in Fig. 4.

The bimolecular decay reaction of aryldiazenyl radicals proceeds in a small volume section at l_i of the solution, thereby we assumed no diffusion of the radicals out of or into the section l_i.[11]

For the second order reaction in section l_i we can apply the equations

$$-\mathrm{d}(\mathrm{R}\cdot_i)/\mathrm{dt} = 2\cdot k_2\cdot(\mathrm{R}\cdot_i)^2 \tag{1}$$

and

$$1/(\mathrm{R}\cdot_i)_t - 1/(\mathrm{R}\cdot_i)_o = 2\cdot k_2\cdot t, \tag{2}$$

where $(\mathrm{R}\cdot_i)_o$ and $(\mathrm{R}\cdot_i)_t$ stand for radical concentrations in the section l_i at time 0 and t, respectively.

On summation of $(\mathrm{R}\cdot_i)$ over all sections at l_i, we get total radical concentration $(\mathrm{R}\cdot)_o$ and $(\mathrm{R}\cdot)_t$ at time 0 and t, respectively, i.e.,

$$(\mathrm{R}\cdot)_o = \sum_{l_i}(\mathrm{R}\cdot_i)_o$$

and

$$(\mathrm{R}\cdot)_t = \sum_{l_i}(\mathrm{R}\cdot_i)_t \tag{3}$$

We observed experimentally the decay process of $(\mathrm{R}\cdot)_o$ from time 0 to ∞, as illustrated in Fig. 5.

The initial radical distribution, $(\mathrm{R}\cdot_i)_o$, can be expressed by Eq. 4, assuming that the aryldiazenyl radicals were produced from diazene by photolysis:

$$(\mathrm{R}\cdot_i)_o = (\mathrm{R}\cdot_o)_o\cdot\exp(-2.30\cdot\varepsilon\cdot c\cdot l_i), \tag{4}$$

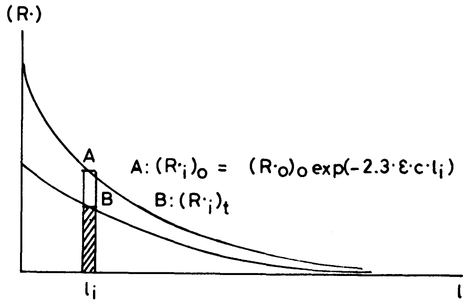

Fig. 4. Exponential distribution of concentration of aryldiazenyl radicals in solution.

where $(\mathrm{R}\cdot_o)_o$ denotes the initial radical concentration at time 0 in the section at l_o, ε the molar absorption coefficient of the starting compound aryl(arylthio)diazene at wavelength 337 nm, $6.5\cdot10^3\ \mathrm{M\,cm^{-1}}$ for (4-*t*-butylphenylthio)phenyldiazene, and c the concentration of the diazene.

The radical concentration at time t, $(\mathrm{R}\cdot)_t$, can be expressed in terms of $(\mathrm{R}\cdot_i)_o$, by using Eqs. 2 and 3 as follows:

$$\begin{aligned}(\mathrm{R}\cdot)_t &= \sum_{l_i}(\mathrm{R}\cdot_i)_t \\ &= \sum_{l_i}[1/\{1/(\mathrm{R}\cdot_i)_o+2\cdot k_2\cdot t\}].\end{aligned} \tag{5}$$

Equation 5 was transformed by integration into Eq. 6,

$$(\mathrm{R}\cdot)_t = \frac{\ln\{1+2\cdot(\mathrm{R}\cdot_o)_o\cdot k_2\cdot t\}}{2\cdot30\cdot2\cdot\varepsilon\cdot c\cdot k_2\cdot t}, \tag{6}$$

which was changed by approximation using the first 3 terms of the Maclaurin Expansion into

$$(\mathrm{R}\cdot)_t = \frac{(\mathrm{R}\cdot_o)_o}{2.30\cdot\varepsilon\cdot c\cdot\{1+(\mathrm{R}\cdot_o)_o\cdot k_2\cdot t\}}, \tag{7}$$

or into Eq. 8,

$$1/(\mathrm{R}\cdot)_t = 2.30\cdot\varepsilon\cdot c/(\mathrm{R}\cdot_o)_o + 2.30\cdot\varepsilon\cdot c\cdot k_2\cdot t, \tag{8}$$

when $1 \gg 2\cdot(\mathrm{R}\cdot_o)_o\cdot k_2\cdot t$.[12] On plotting $1/(\mathrm{R}\cdot)_t$ against time, we can obtain k_2.

In the flow method using a $4\cdot10^{-4}$ M solution of diazene we assumed a homogenous distribution of radicals throughout the irradiated solution and the volume of the solution was taken as one half of the outer sphere in the sample tube (Fig. 6).

The rate constants were calculated by using Eq. 9 of the second order decay reaction.

$$1/(\mathrm{R}\cdot)_t - 1/(\mathrm{R}\cdot)_o = 2\cdot k_2\cdot t \tag{9}$$

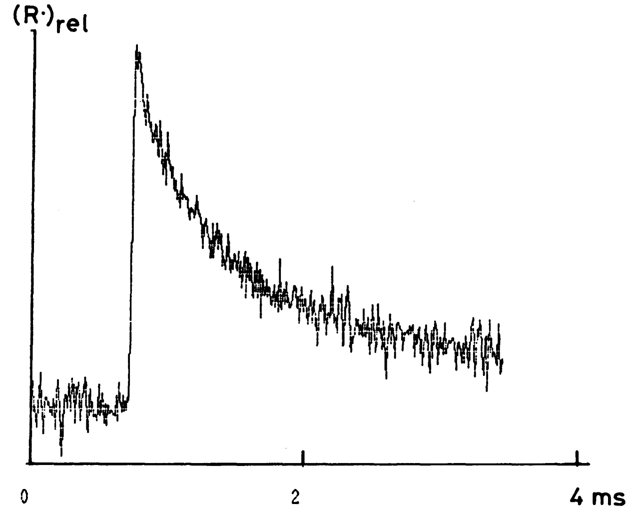

Fig. 5. Second-order decay curve of phenyldiazenyl-d_5 radicals, at $-102\,^\circ$C in $2\cdot10^{-2}$ molar diazene in cyclopropane. Batch method.

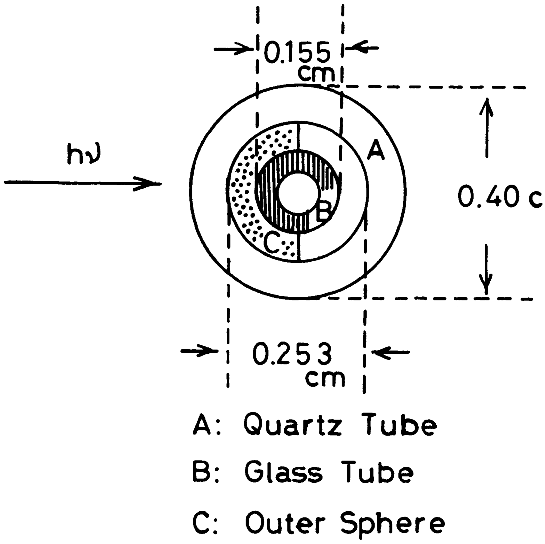

Fig. 6. Aryldiazenyl radicals formed in the outer sphere of sample tube.

It was determined that the effect of k_1 was negligible in the calculation of k_2.

c) Calibration Curve for Determination of the Radical Concentration. As a standard solution of known concentration of free radicals we used solutions of pure nitrosodisulfonate in slightly ammoniacal aq. solution. It was thereby assumed that the line shape of the ESR spectrum of aryldiazenyl radicals was the same as that of nitrosodisulfonate and that the sensitivity of the ESR apparatus was kept constant for free radicals even though the solvent for the radicals was changed from water (nitrosodisulfonate) to a variant of organic solvent (aryldiazenyls).

One line of the triplet of ESR spectrum of nitrosodisulfonate of $0.4\cdot10^{-9}$ to $1.6\cdot10^{-9}$ mol was determined by averaging 20 runs at 25 °C and then double-integrated digitally. A linear correlation of the spectrum peak height to the integrated value was obtained. The conditions of ESR spectrometer for the measurement of calibration curve were set to those for the time-resolved ESR experiment in microwave power, modulation amplitude, and receiver gain.

The kinetic studies were performed at low temperatures and so it was necessary to correct the signal intensity. The increase in intensity was assumed to be proportional to $1/T$ and the signal heights were corrected by multiplying $T/298$.

Results and Discussion

To understand the decay kinetics of aryldiazenyl radicals, it is plausible to describe the following Scheme 1: Aryl(arylthio)diazene was decomposed photochemically to yield aryldiazenyl–arylthiyl radical pair, and then proceeded two reactions, k_{comb} and k_{diff}, in competition. Thereafter occured bimolecular and unimolecular reactions in the solution.

$$\text{Ar-N=N-S-Ar}' \xrightarrow{h\nu} \overline{\text{Ar-N=N}\cdot\ \cdot\text{S-Ar}'} \qquad (10)$$

$$\overline{\text{Ar-N=N}\cdot\ \cdot\text{S-Ar}'} \xrightarrow{k_{\mathrm{comb}}} \text{Ar-N=N-S-Ar}' \qquad (11)$$

$$\text{or}\quad \text{Ar-S-Ar}' + \text{N}_2 \qquad (12)$$

$$\xrightarrow{k_{\mathrm{diff}}} \text{Ar-N=N}\cdot + \cdot\text{S-Ar}' \qquad (13)$$

$$2\ \text{A-N=N}\cdot \xrightarrow{k_2} \text{Ar-N=N-Ar} + \text{N}_2$$

$$\text{or}\quad \text{Ar-Ar} + 2\text{N}_2 \qquad (14)$$

$$\text{Ar-N=N}\cdot + \cdot\text{S-Ar}' \xrightarrow{k_{\mathrm{term}}1} \text{Ar-S-Ar}' + \text{N}_2 \qquad (15)$$

$$2\ \text{Ar}'\text{-S}\cdot \xrightarrow{k_{\mathrm{term}}2} \text{Ar}'\text{-S-S-Ar}' \qquad (16)$$

$$\text{Ar-N=N}\cdot \xrightarrow{k_1} \text{Ar}\cdot + \text{N}_2 \qquad (17)$$

Scheme 1.

Aryl radicals formed in Reaction 17 react with solvent molecules, affording stable products and secondary radicals.

The bimolecular reactions of aryldiazenyl radicals, Reactions 14 and 15, became measurable at the initial period of decay process, when the radical concentrations were high enough or on occasions of slow unimolecular decay of aryldiazenyl radicals by lowering the reaction temperature.

Arylthiyl radicals formed photochemically in 10^{-2} molar diazene solution disappeared in a half-life of several microseconds at −100 °C, which we could follow by measuring the transient UV absorption around 450 to 550 nm of arylthiyl radicals.[13] We can therefore neglect Reaction 15 in calculation of the second order reaction rate of aryldiazenyl radicals. In dilute solutions of 10^{-4} molar aryldiazenes the reaction 15 may cause an effect in k_2 measurements.

(1) First Order Reaction Rate. a) Rate Constant of Phenyldiazenyl-d_5 Radicals. The first order decay rates of aryldiazenyl radicals were obtained by using a 100 kHz modulation ESR spectrometer. The decay curves were analyzed by plotting $\ln\{(\mathrm{R}\cdot)_0/(\mathrm{R}\cdot)_t\}$–time and $1/(\mathrm{R}\cdot)_t$–time to separate the first order reaction from the second-order decay process. The first order rate constants so obtained are listed in Table 2 and Arrhenius Plot of k_1 of some aryldiazenyl radicals is reproduced in Fig. 7.

Aryldiazenyl radicals are relatively persistent and the first order rate constant of phenyldiazenyl-d_5 radical was $34\,\mathrm{s}^{-1}$ at −96 °C. Porter and his coworkers[4] have estimated the rate of decomposition of the order of 10^7 to $10^9\,\mathrm{s}^{-1}$ at 40 °C for phenyldiazenyl radical from the analysis of CIDNP experiment of phenyl(1-methyl-1-phenylethyl)diazene. Another estimation from CIDNP of the half-life of phenyldiazenyl was reported by Kasukhin and colaborators[5] as $t_{1/2}=10^{-7}\,\mathrm{s}$ ($k_1 \fallingdotseq 7\cdot10^6\,\mathrm{s}^{-1}$) at 60 °C.

Our rate constant of phenyldiazenyl-d_5 was extrapolated to +60°C to afford $k_1=4.8\cdot 10^5\ \mathrm{s}^{-1}$. This value was by far lower than the values estimated from CIDNP experiments.

At lower temperatures when the unimolecular decay became slower, bimolecular decay reactions proceeded at the initial period of the decay: The bimolecular reactions were observed at −87 °C for 4-methoxyphenyldiazenyl radicals, at −96 °C for 4-methylphenyldiazenyl radicals, and even at −73 °C for 4-dimethylaminophenyldiazenyl radicals, which were the most persistent radicals among those we studied.

b) Substituent Effect on the First Order Reaction Rate of Aryldiazenyl Radicals. The first order rate constants of 20 aryldiazenyl radicals at −96 °C were plotted against the Hammett sigma constants for 3- and 4-substituted phenyldiazenyl radicals and against the values equivalent to sigma value for 2-substituted phenyldiazenyl radicals. The latter "ortho sigma values" were derived from the acid dissociation constants of 2-substituted benzoic acid[14] based on the definition of the Hammett sigma constant.

For 2-methylthio substituent, the "sigma value" was calculated from σ_p by means of Eq. 18, presented by

Table 2. First Order Rate Constants of Aryldiazenyl Radicals in Cyclopropane, k_1/s^{-1}

Temp/°C	4-Me$_2$N	4-MeO	4-Me	3,5-Me$_2$	3-Me	d_5	2,4,6-Me$_3$	4-Cl	4-Br	4-I
−48	390									
−56	193									
−65	91									
−70		86			530					
−73	16					540	290			
−78		26	100							
−80						140				
−82							154			295
−87		8.7	44	160	80	90			195	
−91							74			104
−96			11	58	21	34		61	48	
−99										41
−104				19		17		30		
−108										
−113								9		
−117										
E_a/kJ mol^{-1}	46.0	42.3	35.6	33.1	38.5	29.7	23.4	26.8		32.2
$\frac{\log A}{\mathrm{s}^{-1}}$	13.21	12.77	11.54	11.49	12.65	10.31	8.55	9.76		11.30
σ-Value	−0.88	−0.28	−0.18	−0.14	−0.07	0.00	0.24	0.23	0.23	0.18

Temp/°C	2-Me	2-MeO	2-MeS	3-MeO	4-CN	3-CH$_3$CO	3-CN	2-F	2-Cl	2-Br
−48										
−56										
−65										
−70										
−73										
−80										
−82	140									
−87										
−91	84	215	80							
−96				70	114	260	352			
−99	36	77	30		84		250	300	700	1200
−104		21		33				101	220	370
−108	14									
−113				8.8						
−117								29	60	93
E_a/kJ mol^{-1}	22.2	34.3		29.3				29.7	31.0	32.2
$\frac{\log A}{\mathrm{s}^{-1}}$	8.26	12.20		10.44				11.31	12.17	12.79
σ-Value	0.68	0.23	0.40	0.12	0.66	0.38	0.56	0.92	1.12	1.16

Yoshida and Hojo[15]

$$\sigma_o = 0.72 + 1.91\cdot\sigma_p \qquad (18)$$

The rate constants of aryldiazenyl radicals correlated linearly to sigma values with $\rho=+1.53$ ($r=0.91$). We did not find any evidence for the extra stabilization effect of 2- and 4-substituents nor extra acceleration effect by the 2-substituents on the decomposition reaction. The fairly linear nature of the Hammett plot is a characteristic feature of aryldiazenyl radicals and stands in a clear contradictory to those of aryldiazonium ions.[16] In the diazonium ions the mesomeric effect of substituents at 2-and 4-positions of the benzene ring, regardless of electron-releasing and electron-withdrawing natures, retarded the decompositions.

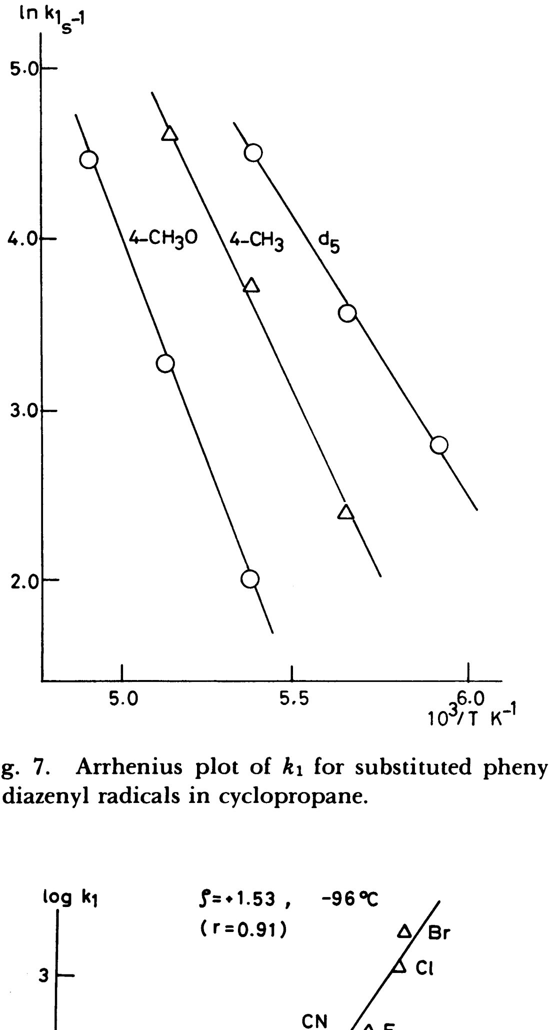

Fig. 7. Arrhenius plot of k_1 for substituted phenyldiazenyl radicals in cyclopropane.

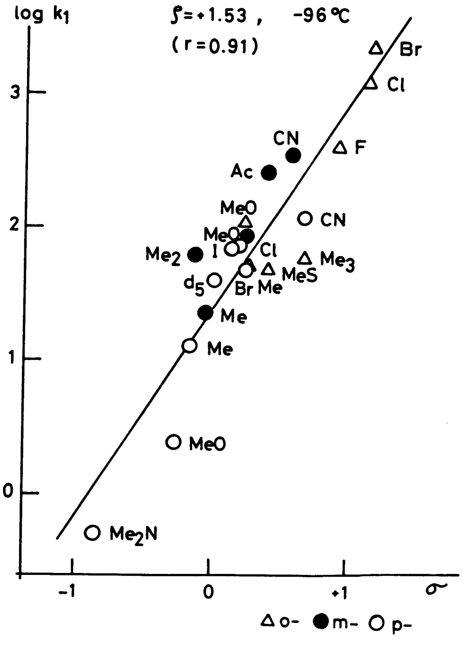

Fig. 8. Hammett plot of k_1 for substituted phenyldiazenyl radicals at −96 °C in cyclopropane.

The positive reaction constant, +1.53, implies a stabilization effect of electron-releasing substituent groups of aryldiazenyl radicals, polarizing thereby negatively at the -N=N group. The INDO calculation[8] suggested also a polar nature of the radicals with a dipole moment of ca. 2.8.

The negatively polarized -N=N group evokes an electrophilic property of aryldiazenyl radicals in their unimolecular decomposition in a variant of solvents. This became true in the determination of rate constants in olefinic solvents.

c) Solvent Effect on the First Order Reaction Rate. The effect of solvent on the rate of the unimolecular decomposition of 4-methoxyphenyldiazenyl radical was studied at −87 °C by using, i) inert hydrocarbon solvents, and ii) olefinic solvents, both in neat or in a 1 : 1 (volume) mixture of cyclopropane.

i) Inert Hydrocarbon Solvent. In inert hydrocarbon of higher molecular weight, such as 2,2,4-trimethylpentane, methylcyclopentane, and toluene in a 1 : 1 mixture of cyclopropane, the unimolecular decay rate of 4-methoxyphenyldiazenyl radical increased by a factor of 2 to 3, independent of the aliphatic or aromatic nature of the solvents. The increase in rate, effected by 2,2,4-trimethylpentane, must be due to viscosity of the solvent, and the effect caused by the trimethylpentane exceeded that of

Table 3. First Order Rate Constant of 4-Methoxyphenyldiazenyl Radical in 1 : 1 Mixture with Cyclopropane at −87 °C

Solvent added	k_1/s^{-1}	$E_a/\text{kJ mol}^{-1}$	$\frac{\log A}{\text{s}^{-1}}$
None	8.7	42.3	12.77
2,2,4-Trimethylpentane	23	—	—
Methylcyclopentane	12	—	—
Toluene	9.3	—	—
1-Butene	73	—	—
cis-2-Butene	62	34.7	12.69
Ethoxyethene	60	39.7	12.86
Propene	42	—	—
Bromoethene	35	—	—
1-Chloropropene	26	—	—

toluene, i.e., hydrogen abstraction reaction by 4-methoxyphenyldiazenyl radical from the methyl group of toluene was probably not important at these low temperatures.

ii) Olefinic Solvents. Olefinic solvents on the other hand accelerated the decay rate of 4-methoxyphenyldiazenyl radicals remarkably. An effect other than that of viscosity must be important. The rate constants in olefinic solvents are listed together with those in hydrocarbon solvents in Table 3.

In 1-butene or *cis*-2-butene neat, we could observe the same ESR spectrum of 4-methoxyphenyldiazenyl radical as that in cyclopropane solution (Fig. 9). This result supports strongly that we are studying the primary radicals formed by photolysis of aryl(arylthio)diazenes and not the radical derived secondarily by some addition reaction of a radical to the starting diazenes.

The increase in rate effected by olefinic solvents is probably caused by a reaction between aryldiazenyl radical and the olefin molecule in a manner such as π-complexing, but not by addition reaction of aryldiazenyl radicals to olefinic double bond.

The minor roll of this addition reaction was deduced from a product study of photolysis of (4-*t*-butylphenylthio)(4-methoxyphenyl)diazene in propene at −78 °C. The reaction products were analyzed by using GC, HPLC, TLC, and NMR techniques, and identified as **a**: anisole (15%), **b**: 4-methoxyphenylpropane (6%), **c**: 4-*t*-butylphenyl 4-methoxyphenyl sulfide (in a small yield), **d**: 4,4′-di-t-butyldiphenyl disulfide (in an appreciable yield), and **e**: probably 2-(4-*t*-butylphenylthio)-1-(4-methoxyphenyl)propane (in a high yield). The compounds **d** and **e** decomposed seriously under the GC conditions. Aryldiazenyl radicals were transformed into dediazoniated products in the main routes of the reactions and this suggested that the dediazoniation was the first step of the reaction of aryldiazenyl radicals.

The mechanism of dediazoniation of aryldiazenyl radicals in olefinic solvents resembles the molecular mechanism of perbenzoic acid in methyl methacrylate⁽¹⁷⁾ and proceeds probably through a formation of complex between aryldiazenyl radical and olefinic linkage under charge transfer from olefinic double bond to diazenyl nitrogen, followed by dediazoniation. The Hammett correlation of the decay rate of 4-methoxyphenyldiazenyl radical to the substituent constants of olefins, $\rho \fallingdotseq -1.0$, although of a poor linearity, and the decrease in activation energy in olefinic solvents, both support a mechanism of dediazoniation accelerated by charge transfer, and this is parallel to the substituent effect in the unimolecular rate constant of aryldiazenyl radicals in cyclopropane: Aryldiazenyl radicals are the more labile, the more neutral the -N=N groups in the radicals are (Fig. 10).

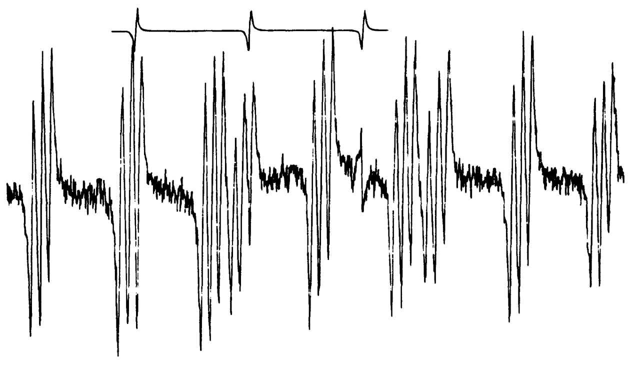

Fig. 9. ESR spectrum of 4-methoxyphenyldiazenyl radicals in 1-butene neat.

d) Possible Reaction Sequence of Unimolecuar Decomposition of Aryldiazenyl Radicals. The characteristic feature of k_1 of aryldiazenyl radicals is the very low frequency factor and the low activation energy, log A=12.8 to 8.3 s^{-1} and E_a=46 to 25 kJ mol^{-1}, respectively. The nature of this is not clear as yet, but can be probably explained by collision activation: aryldiazenyl radicals are activated by collision in a specific configuration, followed by decomposition. The sequence of the processes may be expressed as Eq. 19,

$$\mathrm{d} + \mathrm{m} \underset{k_r}{\overset{k_f}{\rightleftharpoons}} \mathrm{a} + \mathrm{m} \xrightarrow{k_{\mathrm{spontan.}}} \text{products} \tag{19}$$

where a denotes aryldiazenyl radicals in activated state and d those in the ground state. The symbol m stands for the second molecule of collision, usually solvent molecule. When k_f is rate-determining, then k_1 can be expressed as

$$k_1 = k_f \cdot (\mathrm{m})$$

and the rate should be of low frequency factor and dependent on solvent properties. Depolarization of aryldiazenyl radical would be the key step in the decomposition of the radical.

(2) Second Order Reaction Rate. a) Second Order Rate Constant of Phenyldiazenyl-d_5 by Batch Method. In the batch method a cyclopropane solution (2 ml) of $2 \cdot 10^{-2}$ M of aryl(arylthio)diazene was sealed in sample tube in vacuum. After 300 pulse irradiations the irradiated solution in the quartz cell-tube was refreshed by mixing with that of the reservoir, keeping

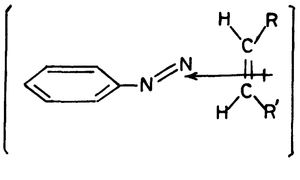

Fig. 10. Charge transfer in the dediazoniation step.

thus the concentration of solution at that of the initial one during the experiment. The rate constants were calculated by using Eq. 8.

The second order decay rates were determined by using 1 MHz modulation technique. A typical decay curve of phenyldiazenyl-d_5 in cyclopropane at −102 °C is reproduced in Fig. 5. The rate constants, k_2, and the Arrhenius parameters are listed in Table 4 and plotted in Fig. 11, respectively.

b) Second Order Rate Constants by Flow Method. In order to examine the rate constants obtained by the batch method using Eq. 8, we measured the rate constant by using more dilute solutions of aryl(arylthio)diazenes $4\cdot10^{-4}$ M in a flow system. In this experiment we used isohexane as solvent instead of cyclopropane because of the low boiling point of cyclopropane and of the low melting point of isohexane.

The concentration of the diazene of $4\cdot10^{-4}$ M, and the depth of the cell solution, 0.048 cm gave an estimation that about 70% of the light intensity irradiated into the solution would pass through unabsorbed and the aryldiazenyl radicals formed were assumed to be homogeneously distributed in the solution. In the calculation of the rate constant we used Eq. 9. The rate constants k_2 of phenyldiazenyl-d_5 in isohexane are listed in Table 5.

The rate constants obtained by the flow method in isohexane were ca. 30 times as high as those obtained by the batch method in cyclopropane, showing the same activation energy. The reason for this difference can be devided in two: 1) the difference of the properties of solvents used, and 2) the conditions for determination of rate constants.

The manuals in the flow method were established as was confirmed by the same rate data by the batch method using isohexane as solvent for $2\cdot10^{-2}$ molar diazene solution as those obtained by the flow method using the isohexane solution of $2\cdot10^{-2}$ M, calculating the rate constant by Eq. 8 for both. The results are shown in Table 6 and in Fig. 11.

The about 3 times higher rate constants by the flow method in isohexane of Table 5 than those by the batch and flow methods in isohexane of Table 6 may arise from the unknown bimolecular side reactions occurring in the more dilute solutions. We believe that the true rate constants are those of the Table 6, judging from 3 points:

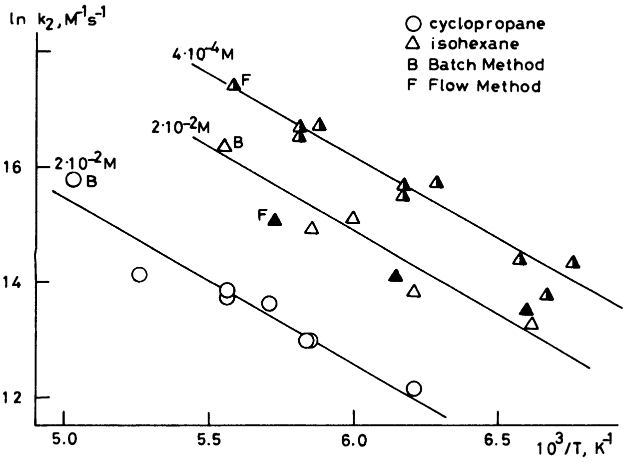

Fig. 11. Arrhenius plots of k_2 for phenyldiazenyl-d_5 radicals. ○: Cyclopropane; △: isohexane; B: batch method; F: flow method.

Table 4. Second Order Rate Constants, k_2, and Arrhenius Parameters of Phenyldiazenyl-d_5 Radical in Cyclopropane, Batch Method, $2\cdot10^{-2}$ M

Temp/°C	k_2/M^{-1}s^{-1}	E_a/kJ mol^{-1}	log A/M^{-1}s^{-1}
−74	$7.3\cdot10^6$	23.4	12.77
−83	$1.4\cdot10^6$		
−93	$9.2\cdot10^5$		
−93	$1.0\cdot10^6$		
−98	$8.2\cdot10^5$		
−102	$4.3\cdot10^5$		
−102	$4.3\cdot10^5$		
−112	$1.9\cdot10^5$		

Table 5. Second Order Rate Constants, k_2, of Phenyldiazenyl-d_5 Radical in Isohexane, Flow Method, $4\cdot10^{-4}$ M

Temp/°C	k_2/M^{-1}s^{-1}	E_a/kJ mol^{-1}	log A/M^{-1}s^{-1}
−94	$3.7\cdot10^7$	24.3	14.58
−101	$1.8\cdot10^7$		
−101	$1.5\cdot10^7$		
−103	$1.9\cdot10^7$		
−111	$6.5\cdot10^6$		
−111	$5.5\cdot10^6$		
−114	$7.1\cdot10^6$		
−121	$1.8\cdot10^6$		
−123	$9.6\cdot10^5$		
−126	$1.7\cdot10^6$		

Table 6. Second Order Rate Constants, k_2, of Phenyldiazenyl-d_5 Radical in Isohexane, Batch and Flow Methods, $2\cdot10^{-2}$ M

Method	Temp/°C	k_2/M^{-1}s^{-1}	E_a/kJ mol^{-1}	log A/M^{-1}s^{-1}
Batch	−93	$1.3\cdot10^7$	24.3	14.02
	−103	$3.1\cdot10^6$		
	−107	$3.5\cdot10^6$		
	−112	$9.9\cdot10^5$		
	−122	$5.9\cdot10^5$		
Flow	−99	$3.4\cdot10^6$		
	−111	$1.3\cdot10^6$		
	−122	$7.4\cdot10^5$		

1) the approximation Eq. 8 of the batch method gives a correct rate constant when the condition, $1 \gg 2\cdot(R\cdot_o)_o\cdot k_2\cdot t$, is satisfied.[12] If not, the equation could give a rate constant about 50% lower than the correct one, and the condition was fulfilled in our experiments. The neglect of the fourth term in the derivation of Eq. 7 can cause only ca. 10% lowering of the rate constant.

2) The estimation of the surface and the volume of the reaction cell in the batch and the flow methods would be too high, may be ca. 2 times. This could give an overestimation of k_2 of ca. 2 times for the both cases.

3) In the flow method using a more dilute radical solution, the apparent rate constant could become higher owing to concurrent radical reactions of aryldiazenyl radicals with other radicals such as arylthiyl radicals, Reaction 15, and with alkylperoxyl radicals formed from peroxide of the solvent molecule when the exclusion of air from the diazene solution was not perfect. We have eliminated the rate data when we have observed traces of peroxyl radicals in the ESR spectrum of aryldiazenyls in the flow method. The accurate amount of the contribution of these concurrent reactions was not clear.

The rate constants in isohexane were about 10 times higher than those in cyclopropane. The accelerating effect of hydrocarbon solvents of higher molecular weight in k_1 is shown in Table 3. We measured k_2 of phenyldiazenyl-d_5 radicals in propane solution at −102 °C to be $9.71\cdot10^5\ M^{-1}\ s^{-1}$ by the batch method. This value was ca. twice as high as that in cyclopropane, $4.3\cdot10^5\ M^{-1}\ s^{-1}$ at the same temperature. Viscosity of the solvent could affect the bimolecular decay rate of aryldiazenyl radicals. The exact nature of the accelerating effect of propane and isohexane was not clear.

The extrapolation of k_2 in cyclopropane by the batch method to 60 °C afforded a value $1.1\cdot10^9\ M^{-1}\ s^{-1}$ which was rather high. We are not in the position to discuss on it now.

c) Substituent Effect in the Second-Order Rate Constants of Phenyldiazenyl Radicals. The second-order rate constants of 4-methoxy-3,5-dideuteriophenyldiazenyl and 4-chloro-3,5-dideuteriophenyldiazenyl radicals were measured by the flow method in isohexane and the results are listed in Table 7.

We found a little increase in activation energy from 21.3 (4-methoxy-3,5-dideuteriophenyldiazenyl) to 24.3 (perdeuteriophenyldiazenyl) to 25.9 (4-chloro-3,5-dideuteriophenyldiazenyl) kJ mol^{-1} but the effect of increase in frequency factors was dominant. The increase in the frequency factor log A, from 13.23 to 14.58 to 15.83 $M^{-1}\ s^{-1}$ was supposed to be due to the increase in the degree of freedom in the activation collision, because the aryldiazenyl radicals are more and more neutral in the -N=N group in the order 4-methoxy- to hydrogen to 4-chloro-substituted phenyldiazenyls and the interaction leading to dediazoniation would be possible from a longer distance in this order.

Table 7. Substituent Effect in the Second-Order Rate Constants of Substituted Phenyldiazenyl Radicals, Flow Method, $4\cdot10^{-4}$ M

Substit. in phenyldiazenyl	Temp °C	k_2 $M^{-1}\ s^{-1}$	E_a kJ mol^{-1}	log A $M^{-1}\ s^{-1}$
4-CH_3O-3,5-d_2	−86	$1.9\cdot10^7$	21.3	13.23
	−97	$8.6\cdot10^6$		
	−107	$3.0\cdot10^6$		
	−117	$1.3\cdot10^6$		
4-Cl-3,5-d_2	−100	$1.1\cdot10^8$	25.9	15.83
	−113	$2.0\cdot10^7$		
	−113	$2.2\cdot10^7$		
	−124	$5.4\cdot10^6$		

For the chemical processes we propose reactions of Eq. 14 for the bimolecular reaction of aryldiazenyl radicals. In accordance with this an emission signal of azoarene was reported in the CIDNP studies of azo compounds.[18]

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11) The diffusion distance of free radical, $D_{R\cdot}$, during the decay period of 1 ms was estimated to be ca. 10^{-2} times as small as the thickness of the radical solution of $1/2.3\cdot\varepsilon\cdot c=3.34\cdot10^{-3}$ cm. The coefficient of disffusion D of CCl_4, for example, at infinite dilution was reported to be $\approx10^{-5}$ cm^2 s^{-1} in cyclohexane at 25 °C, and D decreases by a factor of 40 by lowering the temperature from 25 to −100 °C, as expressed by an experimental equation: $D=2.386\cdot10^{-3}\cdot\exp(-3076\ \mathrm{cal}/RT)$ cm^2 s^{-1} (1 cal=4.184 J), reported by A. F. Collings and R. Mills, *Trans. Faraday Soc.*, **66**, 2761 (1970).

$\bar{D}_{R\cdot}=(2D\cdot t)^{1/2}=(5\cdot10^{-7}\cdot10^{-3})^{1/2}\fallingdotseq2\cdot10^{-5}$ cm.

12) The condition was satisfied when $t\fallingdotseq10^{-3}$ s, $k_2=10^6$—10^7 M^{-1} s^{-1}, and $(\mathrm{R}\cdot_0)_0=10^{-4}$—$10^{-5}$ M, as those found in our experiments, affording $2\cdot(\mathrm{R}\cdot_0)_0\cdot k_2\cdot t=10^{-1}$—$10^{-2}$.

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