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EPR Study of the Kinetics of the Formation of Radicals from Dibenzoyl Peroxide on Porous Glass

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SUMMARY

The kinetics of the formation of radicals from dibenzoyl peroxide supported on porous glass have been determined with EPR techniques over the temperature range of 25-100°C. Values of the activation energy of 18.5 and 25 kcal/mole have been observed for two differently prepared porous glass support materials.

INTRODUCTION

This study was undertaken to determine whether or not it is possible to evaluate the kinetics of the formation of short-lived radical intermediates during thermal decomposition reactions by stabilizing the radicals on porous glass using the technique of Turkevich and Fujita [5] and following the change in intensity of the EPR signals obtained. As described in the experimental section, we have defined conditions under which the radical signal derived from dibenzoyl peroxide can, in fact, be followed over a temperature range suitable for kinetic studies. These conditions, the characteristics of the signals themselves, and the kinetic data (rates and activation energies) derived from the temperature studies over the 30-90°C temperature range are presented in this report.

Prior to the report by Turkevich and Fujita, radicals with lifetimes of only milliseconds or less at room temperature, produced by gamma or UV irradiation, had been observed, but only at very low temperatures, by trapping radicals in a matrix of a frozen solvent and/or by adsorbing them on the surface of silica or alumina [1]. The first EPR spectrum which was ascribed to trapped phenyl radicals was reported by Tolkachev et al. [2], who photolysed phenyl iodide adsorbed on the surface of silica gel at 77°K. Bennett and co-workers [3, 4], who produced phenyl radicals in matrices of frozen solvents by reaction between sodium atoms and iodobenzene in a rotating cryostat at 77°K, obtained the best-resolved EPR spectra and provided definite proof of the existence of phenyl radicals. Turkevich and Fujita [5] were the first to show that methyl radicals produced by photolysis of methyl iodide could be stabilized at room temperature by adsorbing them on porous Vycor glass.

EXPERIMENTAL

Materials

Dibenzoyl peroxide (Fisher reagent grade) was purified by recrystallization from a concentrated chloroform solution by addition of methanol and was carefully dried under vacuum at room temperature. Benzene (Fisher Spectrograde) was used without further purification and was observed to give no EPR signal in the presence of porous glass over the temperature range being used. Vycor porous glass (Corning No. 7930, 96% silica/3% boron oxide; surface area, ca. 144 m^2/g as determined by Turkevich and Fujita [5]) was used as the supporting matrix, in the experiments listed in the accompanying tables, in the form of crushed (>16 mesh) 5-mm rod. Pyrex glass powder (Fisher reagent grade, 200 mesh) was used in several experiments not described herein. Every sample of both of these materials was heated under oxygen, cooled under helium, and tested for absence of an EPR signal before use as a part of each experiment. Vycor glass powder (Corning No. 7930, 100 mesh; pore diameter, 30-45 Å; surface area, 200-350 m^2/g), prepared especially for use in thin-layer chromatography, was used in some experiments. This material was degassed for several hours in vacuo at ca. 100°C before use. Diphenylpicrylhydrazyl (Aldrich Chemical Company) and Varian weak (0.00035%) and strong (0.1%) pitch samples were used in calibration experiments.

Procedure

A carefully weighed (400 or 520 mg) sample of porous glass fragments was placed in a quartz sample tube (5-mm o.d.). This sample tube was attached to a vacuum line system, heated to 200-300°C under oxygen, cooled under helium, evacuated for several hours below 0.01 mmHg, flushed with helium, stoppered, and stored under helium. Samples thus treated are designated as the L (for low temperature) series. In another series of experiments (designated as the H series), the glass sample was heated to a red glow in oxygen for 15 min, during which time the color changed from yellow to dark brown to grey to a clear transparency. Every sample used in each experiment was checked to be EPR signal-free before use. The solution (0.2 ml/400 mg or 0.3 ml/520 mg of glass) of dibenzoyl peroxide in benzene, prepared at the concentrations listed in the tables, was inserted through the septum to the bottom of the sample tube using a calibrated syringe. This was sufficient to just cover the glass. After 15 min the solvent was removed under vacuum and the tube was evacuated below 0.01 mm. The tube was then stoppered under helium and used in the kinetic experiments.

EPR Instrumentation and Techniques

The EPR instrument used in these experiments was a Varian model V-4502-15 spectrometer with a 12-in. magnet, a V-4560 100-kc field modulation unit, a V-4532 dual sample cavity, a V-4257 variable-temperature accessory, and a V-4540 variable-temperature control unit. A recently designed microwave bridge (model 41-B) was used. [The magnetic field was calibrated using a Varian FR-40 digital gaussmeter (Hall effect).] All experiments were carried out in the temperature range between 25 and 100°C with a nitrogen flow rate of 10 ft^3/hr. The specific temperatures used in each experiment as stated in the tables were established at ±3°C (manufacturer's specification). The time reading for each experiment was started 10 min after the temperature control dial was reset (5-65°C gradient) at the desired temperature. The first-derivative spectrum was recorded after the time intervals stated in the tables. The height of the curve was measured in centimeters and corrected for any change in signal level setting for convenient recording of the signal (see Fig. 1 for an example). The signal height increases to a maximum which does not further increase over an extended period (several hours) at room temperature. This signal decreases only slightly over a period of several weeks. Specific operating settings for one of many similar, typical series of experiments are given in the legend for Fig. 1.

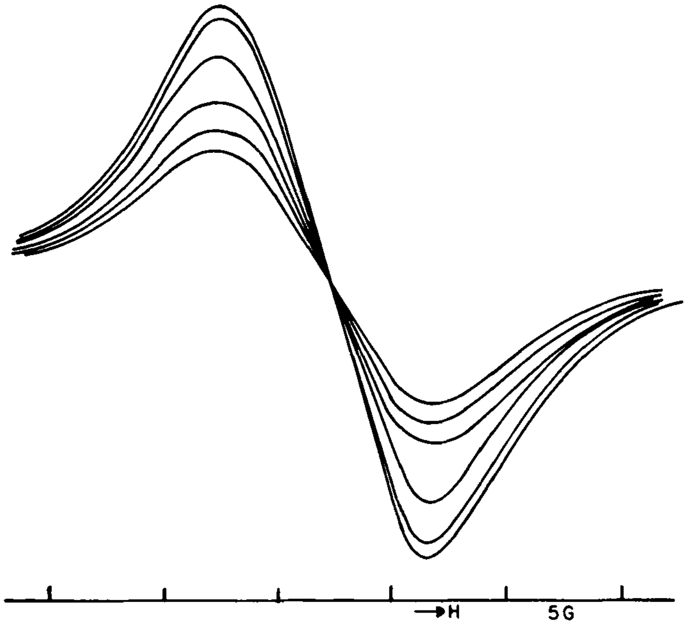

Fig. 1. EPR spectra for benzoyl peroxide on porous glass (L series, Vycor 7930, fragments, experiment No. 4) at 30°C at time intervals and signal heights as follows: 1) 6 min, 45 sec; height, 5.5 cm. 2) 13 min, 30 sec; height, 6.5 cm. 3) 24 min, 30 sec; height, 7.7 cm. 4) 43 min, 45 sec; height, 9.6 cm. 5) 63 min; height, 11.4 cm. 6) 97 min, 40 sec; height, 11.9 cm. Nos. 1-5: signal level, 100; modulation amplitude, 500; filter time constant, 0.1 sec; sweep range, 100 G; sweep time, 10 min; chart speed, 2 in./min; attenuation, 2.5 dial (ca. 6 dB). No. 6: same, except signal level, 63. Scale division, 5 G. Glass series L.

In all runs, the modulation amplitude setting was kept at a level just below that at which line-broadening is observed.

Control and Calibration Experiments

As already noted, the glass matrix for each experiment was checked by EPR examination, prior to depositing benzoyl peroxide thereon, to establish that it gave no EPR signal. The benzoyl peroxide, solid or in benzene solution, gave no EPR signal when heated in the absence of the glass matrix. When measurements in the low-concentration range and low temperatures

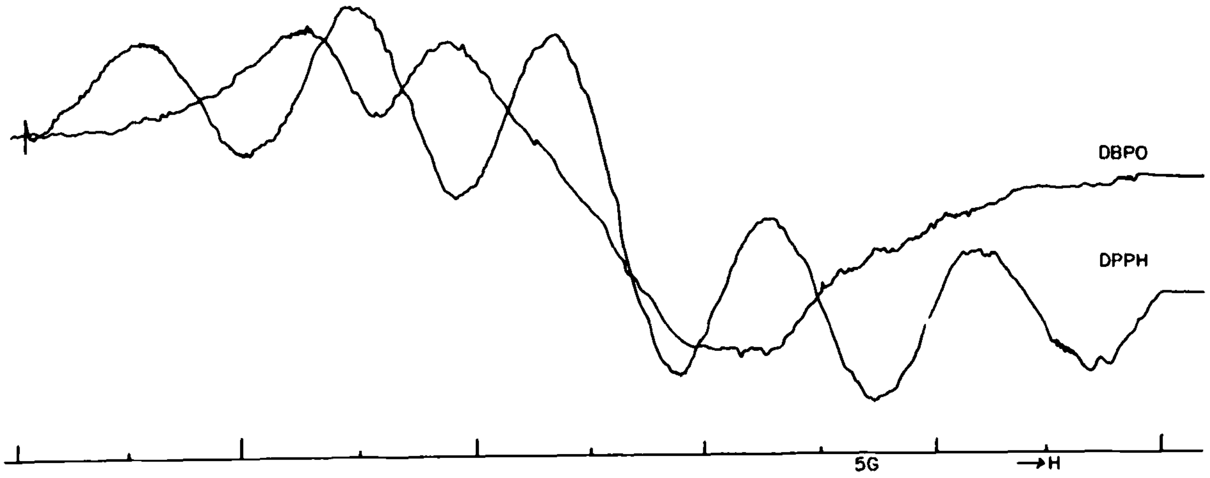

Fig. 2. EPR spectra for benzoyl peroxide on porous glass (Vycor 7930, fragments) at 25°C. Initial reading showing both weak and strong signal prior to change of former to shoulder and disappearance. Signal level, 500; modulation amplitude, 500; filter time constant, 3.0 sec; sweep range, 100 G; sweep time, 10 min; chart speed, 2 in./min; attenuation, 2.5 dial (ca. 6 dB). Scale division, 5 G.

listed in the tables were used, an additional weak signal (Fig. 2) was observed which could not be used for kinetic evaluation.

The level of reproducibility in these experimental techniques has been evaluated in several series of replicate experiments. Data for triplicate experiments at 70°C in the H series, using glass support samples prepared simultaneously, and thus identically, are given in Table 3. These data show a deviation of ±10% in the rates. A similar set of data for the L series, given in Table 4, shows a deviation of ±15% in the rates for a series of triplicate experiments at 50°C. Samples of glass support prepared in different batches instead of simultaneously showed deviations of ±15% for the H series (footnote g, Table 3). Different glass samples in the L series gave values for the relative rates varying over a 100-200% range but gave what appear to be comparable temperature dependencies and activation energies within a given series. Experiments with amounts of benzoyl peroxide varying from 0.25 to 8.0 mg/400 mg of glass (H series) and from 0.41 to 8.33 mg/520 mg of glass (L series) showed rates which reached a maximum in the 1- to 2-mg range. Amounts in this range were then used in temperature dependency measurements.

The intensity of the peroxide-derived signal was compared with that of a standard sample of the same diameter (Varian 904450-01, 0.1% pitch on potassium chloride) and of known (3×10^{15} spins/cm) spin concentration. The highest spin concentration of stabilized radicals observed in our experiments is estimated at about 2.5×10^{14} spins/cm.

RESULTS

The EPR spectrum obtained in our experiments, using dibenzoyl peroxide on porous glass, shows two signals. A typical absorption pattern showing these two signals of different intensity is given in Fig. 2. The more intense signal is about 8 G in width, occurs at approximately the same field strength as diphenylpicrylte hydrazyl with a g value of about 2.0036, is observed at a temperature of 30-90°C, and has an approximate Lorentzian shape. This signal increases with time up to a limiting value dependent in intensity on the initial ratio of the peroxide to glass support. A typical series of spectra are given in Fig. 1. The less intense signal is observed only at temperatures below 60°C and at low peroxide concentrations, as shown in Fig. 2. This weak signal, in some cases originally nearly as intense as the stronger signal, has a line width of 3G with a g value of about 1.996; it slowly decreases with time and disappears from the spectrum both after a time interval and if heated above 60°C. Neither signal shows any hyperfine splitting under any conditions we have used. The strong signal is suitable for kinetic measurements; the weaker signal is not.

The kinetic data for two series of experiments are given in Tables 1-4 and Figs. 3-6. These experiments involve a range of relative amounts of dibenzoyl peroxide deposited in the porous glass support varying from 0.20 to 8.0 mg of dibenzoyl peroxide/400 mg of glass (1/2500 to 1/50). In each experiment the intensity of the signal at 2.0036 G increases linearly with time over a 1- to 2-hr period after thermal equilibrium is established. The slopes of these lines (Figs. 3-6) give relative rates which vary from 0.6 to 28.0. The two series (H and L) of data (Tables 1-4) involve experiments for which the powdered glass was heated to different temperatures, as described in the experimental section, to destroy possible organic contaminants which might give a spurious EPR signal. The H series gave reasonably reproducible rate results; the deviation is ±10%, as shown in the data in Table 3 for experiments at 70°C using uniform glass samples (footnote h). Data from different glass sample preparations show greater deviations. Data for

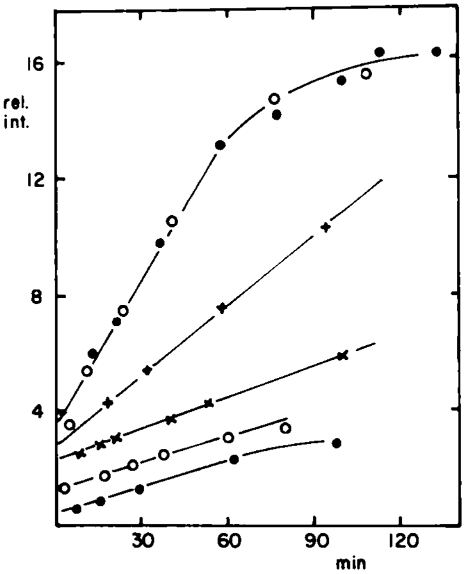

Fig. 3. Rate of increase in intensity of EPR signal for H series of experiments at 80°C and with various ratios (0.25-8.0 mg/400 mg) of benzoyl peroxide to glass. Data from Table 1.

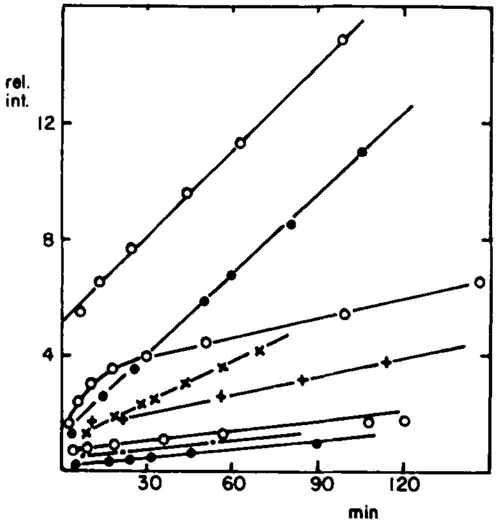

Fig. 4. Rate of increase in intensity of EPR signal for L series of experiments at 30°C and with various ratios (0.2-8.33 mg/520 mg) of benzoyl peroxide to glass. Data from Table 2.

triplicate experiments in the L series at 50°C using uniform glass samples show ±15% deviations (Table 4). The relative rates are higher for the glass heated to low temperature and are reproducible only within one series of experiments. The activation energies for the two series of experiments, calculated from the slopes of the intensity-time plots at different temperatures and the Arrhenius equation, are 25 kcal/mole (H series) and 18.5 kcal/mole (L series).

DISCUSSION

Interpretation of the EPR Spectra

Assuming that dibenzoyl peroxide decomposes in the adsorbed state as it does in homogeneous systems, evidence for two radicals—phenyl and benzoyloxy—should be obtainable in appropriate EPR experiments. The decomposition of benzoyl peroxide in various homogeneous systems has been studied extensively over the past 40 years [6-13]. The decomposition products obtained in the presence of iodine as an inhibitor [10, 13], in the absence of any solvent [12], and in the presence of polymerizable monomers

Table 1. Kinetic Data for the Decomposition of Dibenzoyl Peroxide on Porous Glass[a] (H Series) at 80°C and with Various Ratios of Peroxide to Glass

Benzoyl peroxide[b]	0.25		0.50		1.0		2.0		4.0		8.0	
Time[c]/relative intensity[d]	7:40	2.52	18:00	4.3	5:00	3.48	12:30	6.0	7:00	0.64	2:00	1.32
	15:00	2.80	32:00	5.4	11:00	5.4	22:35	7.25	14:45	0.92	16:00	1.76
	20:00	2.96	58:00	7.55	23:00	7.4	37:00	9.8	29:00	1.34	26:30	2.16
	40:00	3.65	94:00	10.3	41:30	10.5	57:00	13.2	61:00	2.32	38:00	2.44
	54:00	4.20			76:35	14.7	77:00	14.2	97:30	2.80	60:10	3.10
	100:00	5.70			108:00	15.6	102:00	15.4			80:00	3.40
							132:00	16.4				
Relative rate[e]	3.85		8.2		16.4		16.4		3.32		3.50	

[a] Vycor porous glass (No. 7930) heated under vacuum to ca. 400°C; each sample EPR signal-free.

[b] mg/400 mg of glass.

[c] In minutes.

[d] Relative intensity of absorption: signal height observed/signal level used × 100 to adjust to uniform signal level.

[e] Relative rate: slope (dI/dt) of time conversion plot; from Fig. 3.

Table 2. Kinetic Data for the Decomposition of Debenzoyl Peroxide on Porous Glass[a] (L Series) at 30°C and at Various Ratios of Peroxide to Glass

Benzoyl peroxide[b]	0.2		0.41		0.8		1.5		1.67		3.33		6.0		8.33	
Time[c]/relative intensity[d]	3:30	2.4	4:00	1.02	6:45	5.5	3:30	1.5	3:00	1.63	4:00	0.64	4:30	0.26	2:10	0.44
	10:20	3.04	9:10	1.44	13:30	6.5	14:30	2.64	10:30	1.70	4:00	0.76	17:20	0.36	8:00	0.58
	18:00	3.52	18:30	1.84	24:30	7.7	26:00	3.6	21:00	1.83	19:00	0.86	24:00	0.44	20:45	0.71
	30:30	3.96	28:00	2.3	43:45	9.6	50:15	5.94			36:00	1.12	31:00	0.48	54:00	1.04
	51:00	4.45	44:00	2.52	63:00	11.4	59:00	6.8	56:00	2.56	56:30	1.20	45:00	0.68	90:00	1.42
	99:25	5.4	56:00	3.64	97:40	14.9	80:00	8.5	85:00	3.15	108:00	1.66	90:00	0.98		
	147:00	6.56	70:00	4.17	162:00	18.2	105:00	11.1	114:00	3.76	121:00	1.68				
Relative rate[e]	2.3		4.7		9.4		9.3		2.0		1.3		1.0		1.0	

[a] As in Table 1, footnote a; glass heated to ca. 300°C.
[b] mg/520 mg of glass.
[c] In minutes.
[d] As in Table 1, footnote d.
[e] As in Table 1, footnote e; from Fig. 4.

Table 3. Kinetic Data for Decomposition of Dibenzoyl Peroxide[a] on Porous Glass[b] (H Series) at Temperatures of 60-90°C

Temperature[c]	Time[d]/relative intensity[e]					Relative rate[f]
60	26:00/0.54	58:00/0.80	93:00/0.96	127:30/1.16	150:00/1.32	0.6
70[g]	30:00/0.70	55:00/1.24	62:00/1.40	77:00/1.76	116:00/2.68	2.3
70[g]	19:00/2.8	36:30/3.28	56:00/3.8	92:20/4.8		2.7
70[h]	8:00/1.76	17:10/1.98	30:40/2.28	53:70/2.78	66:00/3.06	2.2
70[h]	6:00/2.14	17:00/2.36	42:00/2.92	71:30/3.32	90:00/3.8	2.0
70[h]	19:00/1.52	28:10/1.70	33:40/1.80	48:00/2.04	81:00/2.64	
	101:00/3.02					1.8
80	17:00/1.00	35:00/2.00	39:00/2.20	48:00/2.76	64:00/3.62	
	84:00/4.80					
90[g]	5:00/1.64	10:00/1.80	18:00/2.32	31:10/3.96	40:20/5.20	5.8
	47:00/6.30	66:00/8.20	94:30/9.6			13.0
90[g]	13:00/6.0	22:30/7.5	40:00/10.0	71:00/14.8	99:30/17.0	
	148:00/18.2					15.0

[a] Concentration: 2 mg/400 mg of glass.

[b] As in Table 1, footnote a.

[c] Degrees centigrade.

[d] In minutes.

[e] As in Table 1, footnote d.

[f] As in Table 1, footnote e; from Fig. 5.

[g] Duplicate runs at same temperature but with different glass preparations.

[h] Triplicate runs at same temperature and with same glass preparations.

Table 4. Kinetic Data for the Decomposition of Dibenzoyl Peroxide[a] on Porous Glass[b] (L Series) at Temperatures of 40-80°C

Temperature[c]	40		50		50		50		60		70		80	
Time[d]/relative intensity[e]	6:00	1.84	3:20	0.8	4:40	1.44	7:00	0.98	7:10	3.72	5:30	2.16	3:30	1.36
	12:00	2:00	6:45	1.68	14:00	1.84	14:30	1.28	14:30	4.08	11:00	2.80	7:30	2.40
	20:20	2.24	12:30	3.32	22:00	2.16	26:00	1.62	18:45	4.20	21:00	4:30	18:30	6.00
	40:00	2.40	20:30	3.56	26:40	2.36	50:00	2.31	30:30	5.10	35:00	6.50	26:30	8.10
	84:00	2.88	31:30	4.00					49:20	6.40	50:00	9:00	36:30	11.2
	120:00	3.20	53.20	4.70	38:00	2.74	67:00	2.8	84:30	8.75	72:00	12.00	51:30	15.2
	146:00	3.48	89:10	6.00	70:00	4.00	95:00	3.64	89:30	9.40	145:00	14.00	78:00	20.4
	188:00	3.92	145:40	8.20			115:00	4.2	146:30	13.40				
									211:00	20.70				
Relative rate[f]	1.00		3.5		3.9		3.0		7.0		17.0		28.0	

[a] Concentration: 2 mg/400 mg of glass.
[b] As in Table 2, footnote a.
[c] Degrees centrigrade.
[d] In minutes.
[e] As in Table 1, footnote d.
[f] As in Table 1, footnote e; from Fig. 6.

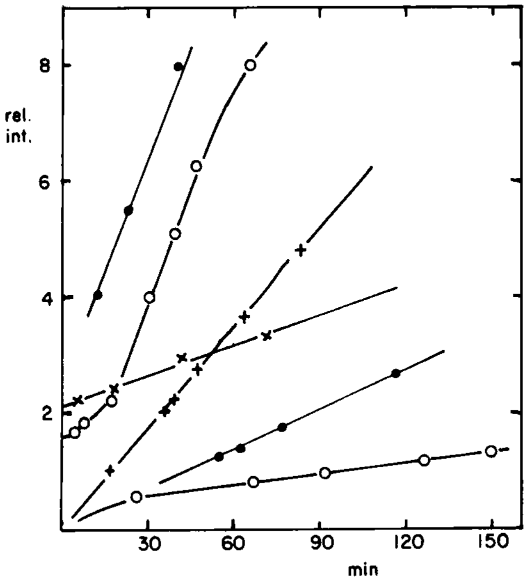

Fig. 5. Rate of increase in intensity of EPR signal for H series of experiments at 2.0 mg of peroxide/400 mg of glass and at 60-90°C. Data from Table 3. ○: 60°C; ●, X: 70°C; +: 80°C; ○, ●: 90°C.

[14-17] establish that the initial reaction involves dissociation to benzoyloxy radicals and that these, on loss of carbon dioxide, give phenyl radicals. EPR observations of such radicals presumably require stabilization either at low temperatures or on porous surfaces, as described by Turkevich and Fujita [5].

In our experiments two EPR signals with different g values have been observed during the decomposition of dibenzoyl peroxide on porous glass in the temperature range of 25-100°C. The first signal is weaker, disappears rapidly, is thermally less stable, and is observed at lower g values than is the second, more stable signal. This first, less stable signal is accordingly thought to be that from the benzoyloxy radical. The thermally stable signal increases in intensity with time and is presumed to be that for the phenyl radical. A complete identification of the two signals was not possible in terms of hyperfine splittings. No hyperfine splitting was observed in any of our experiments. We attribute this to a rigid orientation of the radicals in the matrix such that the anisotropic components of the hyperfine coupling interaction are not averaged out.

It is believed that these observations are consistent with a slow, rate-determining decomposition of the peroxide to form the benzoyloxy radical. The benzoyloxy radical is detectable under favorable circumstances but undergoes relatively rapid decomposition to form the phenyl radical. It is the concentration of the phenyl radical, it is believed, that is being followed as it builds up on the support in our experiment. The benzoyloxy radical should, as is observed, be the low-field signal of the two. The alternative fast decomposition of the peroxide and slow dissociation of the benzoyloxy radical with rapid loss of the phenyl radical, by combination, for example, raises questions that are difficult to answer. For example, it is difficult to see why the benzoyloxy radical, but not the phenyl radical, should be stabilized on the support.

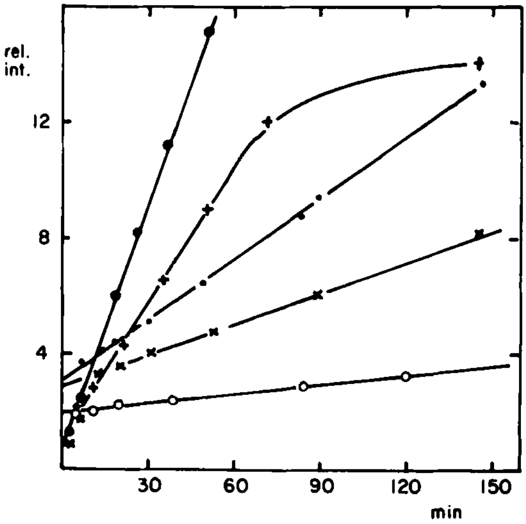

Fig. 6. Rate of increase in intensity of EPR signal for L series of experiments at 2.0 mg of peroxide/400 mg of glass and at 40-80°C. Data from Table 4. o: 40°C; X: 50°C; • : 60°C; +: 70°C; •: 80°C.

Interpretation of the Kinetic Data

It has been assumed for our kinetic analyses that the increase in concentration of the trapped radicals with time is proportional to the rate of decomposition of the peroxide adsorbed on the surface. This implies that the number of radicals adsorbed and stabilized is proportional to the total concentration of radicals formed in the decomposition reaction.

The activation energies usually quoted [18] for the thermal dissociation of benzoyl peroxide are 29-31 kcal/mole for low concentrations of peroxide in inert solvents, and the reaction is first-order unless subject to the induced decomposition reaction. The difference between our observed values of 18.5-25 kcal/mole and the thermal (solution) values of 29-31 kcal/mole may be related to surface adsorption energy, an induced decomposition reaction, a surface catalytic effect, or some combination of effects.

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