column yielded 14.0 ml. of deutero-butanol having $\alpha^{25}\text{D}$ 0.154 ± 0.004° (*l* 2), d^{25}_4 0.8118. The intensity of the C–D band at 2200 cm.$^{-1}$ was compared with that of authentic 1-butanol-1-*d* and indicated the presence of 0.56 deuterium atom per molecule. The density measurement corresponds to 0.54 deuterium atom per molecule, assuming constancy of molecular volume. The 14.0 ml. of this deutero-butanol was diluted with *n*-butyl alcohol to a final volume of 30.0 ml., having $\alpha^{25}\text{D}$ 0.145 ± 0.005° (*l* 4). The deutero-butyl acetate prepared from this alcohol and acetyl chloride and pyridine had $\alpha^{25}\text{D}$ −0.213 ± 0.004° (*l* 2).

BERKELEY, CALIF.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, POLYTECHNIC INSTITUTE OF BROOKLYN]

The Decomposition of Peroxycarbamates and their Efficiency as Initiators in Vinyl Polymerization[1,2]

BY EUGENE L. O'BRIEN, F. MARSHALL BERINGER AND ROBERT B. MESROBIAN[3]

RECEIVED JUNE 28, 1957

t-Butyl and cumyl N-phenylperoxycarbamates have been prepared by the reaction of *t*-butyl and cumyl hydroperoxides with phenyl isocyanate, and *t*-butyl N-α-naphthylperoxycarbamate was prepared by the reaction of *t*-butyl hydroperoxide with α-naphthyl isocyanate. The decompositions of the first two N-phenylperoxycarbamates have been measured in several solvents between 50 and 90° and found to be first-order reactions governed by the specific rate constants $k_d = 1.52 \times 10^{16} \exp(32{,}500/RT)$ and $k_d = 1.26 \times 10^{14} \exp(28{,}100/RT)$, sec.$^{-1}$, respectively. In the case of *t*-butyl N-α-naphthylperoxycarbamate the tendency for induced decomposition is too great to enable an accurate determination of the decomposition rate expression. From polymerization studies of styrene monomer the initiation efficiencies of the N-phenyl derivatives are calculated to be 0.95 and 0.73, respectively, while the N-α-naphthyl derivative shows a wide variation of efficiency with catalyst concentration. Measurements of carbon dioxide evolution in several solvents indicate that nearly one mole of gas is evolved per mole of peroxycarbamate decomposed. Thus, it is concluded that both the *t*-butoxy and the phenylamino radicals from *t*-butyl N-phenylperoxycarbamate efficiently initiate chains while the radicals from the other two peroxycarbamates are less efficient.

It is well known that organic isocyanates react with compounds having active hydrogens to produce addition products. However, not until recent years has the preparation of peroxycarbamates from organic hydroperoxides and isocyanates been reported.[4] This study describes the preparation of three peroxycarbamates and their decomposition in various solvents including styrene monomer. By determination of the efficiency of initiation of styrene polymerization, it is possible to investigate the reactivity of radical intermediates obtained during decomposition.

Experimental[5]

Reagents.—*t*-Butyl hydroperoxide (Lucidol Div., Novadel–Agene Corp.) of 67% purity was added to a 25% solution of sodium hydroxide below 30°. Crystals of the sodium salt of the hydroperoxide were collected and washed twice with benzene. The crystals were then dissolved in distilled water, and the *p*H was adjusted to 7.5. The peroxide was extracted from solution with petroleum ether. *t*-Butyl hydroperoxide of 98% purity was obtained by distilling the petroleum ether under reduced pressure at room temperature. Cumene hydroperoxide was purified by an essentially similar procedure.

Phenyl isocyanate, b.p. 78° at 40 mm., and α-naphthyl isocyanate, b.p. 140° at 12 mm., were obtained by distillation under nitrogen and used immediately. Styrene (Dow Chemical Co.) was washed with 5% aqueous sodium hydroxide, dried over anhydrous magnesium sulfate and distilled under nitrogen; b.p. 40–42° (20 mm.). All other reagents were of highest available purity and were used as received.

***t*-Butyl N-Phenylperoxycarbamate.**—One-tenth mole each of *t*-butyl hydroperoxide and phenyl isocyanate and a few drops of pyridine were dissolved in benzene, and the temperature was maintained at 30°. After 15 minutes the solution became yellow, and the benzene was removed under reduced pressure at room temperature. The product was twice recrystallized from petroleum ether, b.p. 28–38°, to give colorless crystals, m.p. 83° dec., which turned yellow if allowed to stand at room temperature. The peroxycarbamate was stored at Dry Ice temperature.

Alternatively, the hydroperoxide was added to phenyl isocyanate in the presence of pyridine catalyst. After 15 minutes there were formed crystals of the peroxycarbamate, which could be extracted with cold benzene, leaving a residue of *sym*-diphenylurea. The benzene was removed, and the peroxide was recrystallized from petroleum ether.

Iodometric analysis of various samples of the peroxycarbamate indicated 95–97% purity.

Anal. Calcd. for $C_{11}H_{15}NO_3$: N, 6.69. Found: N, 6.64.

Cumyl N-Phenylperoxycarbamate.—Equimolar amounts of phenyl isocyanate and cumene hydroperoxide were placed in a beaker containing 100 ml. of benzene and several drops of pyridine. After 15 minutes, the benzene was removed under reduced pressure at room temperature. The residue was crystallized twice from petroleum ether, b.p. 28–30°, to give a product of m.p. 72°, decomposing at 82°. Iodometric analysis of the compound gave a purity of 95%.

Anal. Calcd. for $C_{16}H_{17}NO_3$: N, 5.16. Found: N, 5.35.

***t*-Butyl N-α-Naphthylperoxycarbonate.**—A solution of one-tenth mole each of *t*-butyl hydroperoxide and α-naphthyl isocyanate, 5 ml. of benzene and a drop of pyridine deposited a solid after 15 minutes. The solid was collected and extracted with petroleum ether, b.p. 28–30°. The insoluble residue was di-α-naphthylurea, m.p. 297–298°. After the extract was cooled to −50° and allowed to warm to 0°, the petroleum ether was removed by decantation from an oily solid, impure *t*-butyl N-α-naphthylperoxycarbonate. The procedure was repeated several times with fresh petroleum ether. The peroxycarbonate as recovered was of 98% purity, as determined iodimetrically.

Anal. Calcd. for $C_{15}H_{17}NO_3$: N, 5.41. Found: N, 5.68.

Procedures.—Solutions of the peroxycarbamates were sealed in ampules that had been deoxygenated by flushing with prepurified nitrogen (Matheson Co.) bubbled through xylene and a solution of benzophenone containing suspended potassium metal. After specified time intervals in a water-bath, aliquots of each ampule were pipetted into 20–30 ml. of glacial acetic acid. After aqueous potassium iodide had

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[1] This work was supported by the Office of Naval Research under Contract N6onr-26309. Reproduction in whole or in part is permitted for any purpose by the U. S. Government.

[2] This paper is taken from a doctoral dissertation of Eugene L. O'Brien.

[3] To whom inquiries about this paper should be sent. Central Research and Engineering Division, Continental Can Co., Inc., 7622 South Racine Ave., Chicago 20, Ill.

[4] A. G. David and K. J. Hunter, *J. Chem. Soc.*, 1808 (1953).

[5] Analyses were performed by the Schwarzkopf Microanalytical Laboratory, Woodside, N. Y.

been added, the procedure of Blomquist and Ferris[6] was employed to titrate the liberated iodine to a starch end-point.

An example of the styrene polymerization follows. Solutions of *t*-butyl N-phenylperoxycarbamate in styrene sealed in ampules as described above were placed in a water-bath at 51 ± 0.02° for 5 hr. The contents of the ampules were then transferred to benzene, and the solution was added dropwise with stirring to a large volume of methanol. Polystyrene was collected on a tared glass filter and dried for 24 hr. at room temperature *in vacuo*.

Molecular weights of the polymer samples were obtained by determining intrinsic viscosities[7] in toluene at 28° and applying the following relation for unfractionated samples.

$$[\eta] = 4.61 \times 10^{-3}\,\bar{P}_n^{0.73} \qquad (1)$$

Carbon dioxide evolved during decomposition of the peroxide in xylene and styrene solvents was measured by a gas buret attached to the reaction flask and containing acidified water (previously saturated with carbon dioxide).

Experimental Results

***t*-Butyl N-phenylperoxycarbamate.**—The rate of decomposition of *t*-butyl N-phenylperoxycarbamate in xylene was studied at four temperatures, and first-order kinetics were observed (Fig. 1).

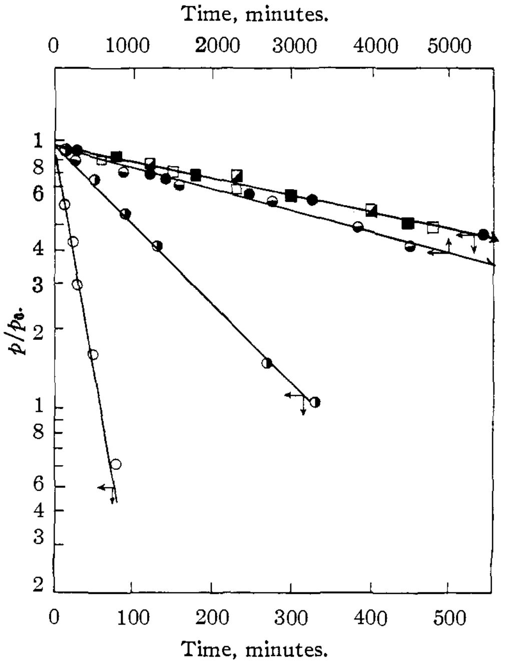

Fig. 1.—Decomposition of *t*-butyl N-phenylperoxycarbamate in xylene at several temperatures. Initial peroxide concentrations at 66.7°: □, 6.00 × 10^{-3} (in chlorobenzene); ■, 6.46 × 10^{-3}; ◩, 7.70 × 10^{-3}; ●, 32.00 × 10^{-3}; at 51.2°: ⊖, 1.22 × 10^{-3}; at 77.7°: ◑, 6.00 × 10^{-3}; at 90.7°: ○, 10.10 × 10^{-3}.

The studies at 67.7° were performed at three different initial peroxide concentrations in order to show that the rate constant was independent of concentration. Comparison of runs at 66.7° in xylene and chlorobenzene demonstrates that solvent polarity has no significant effect. The data of Fig. 1 give the following rate expression for the temperature dependence of the unimolecular rate constant, k_d.

$$k_d = 1.51 \times 10^{16} \exp(-32{,}500 \text{ cal.}/RT) \text{ sec.}^{-1} \qquad (2)$$

The presence of carbon dioxide as a decomposition product was substantiated by gas and infrared analysis. The maximum volume of carbon dioxide evolved at an initial peroxide concentration of 8 × 10^{-4} M in xylene was 90.3% of the theoretical value while in styrene monomer it was 85.4%. Infrared analysis of aliquots of the benzene solution during composition demonstrated a complete disappearance of the carbonyl peak at 5.85 μ.

Figure 2 presents a logarithmic plot of the rate of styrene polymerization, R_p, against catalyst concentration at 50.7°. Table I summarizes the conditions of each experiment.

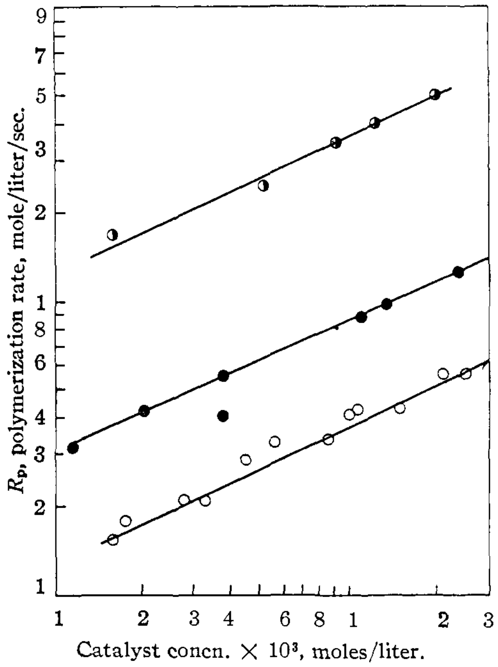

Fig. 2.—Polymerization of styrene: ○, initiated by *t*-butyl N-phenylperoxycarbamate at 50.7°; ●, initiated by cumyl N-phenylperoxycarbamate at 51.0°; ◑, polymerization of methyl methacrylate initiated by cumyl N-phenylperoxycarbamate at 51.0°; slopes: ○, 0.47; ●, 0.45; ◑, 0.47.

R'_1 in Table I is the rate of initiation of polymerization and is determined by equation 4, where the value of A' is taken from the following equation (ref. 6).

$$A' = 5.68 \times 10^{-6} \exp(12{,}460 \text{ cal.}/RT) \qquad (3)$$

$$R'_i = \frac{2A'R_p^2}{(\text{M})^2} \qquad (4)$$

In Table I, f' is the catalyst efficiency determined by equation 5 and is calculated to be 0.95 using values of k_d found by decomposition measurements.

$$R'_i = 2f'k_d\,(\text{catalyst}) \qquad (5)$$

The effect on molecular weight of varying catalyst concentration is reported in Table II and in Figure 3, which shows a slope of 0.51.

In order to determine whether chain transfer of growing styryl radicals to catalyst occurs, the data

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[6] A. T. Blomquist and A. F. Ferris, THIS JOURNAL, **73**, 3214 (1951).

[7] A. V. Tobolsky and J. Offenbach, *J. Polymer Sci.*, **16**, 311 (1955).

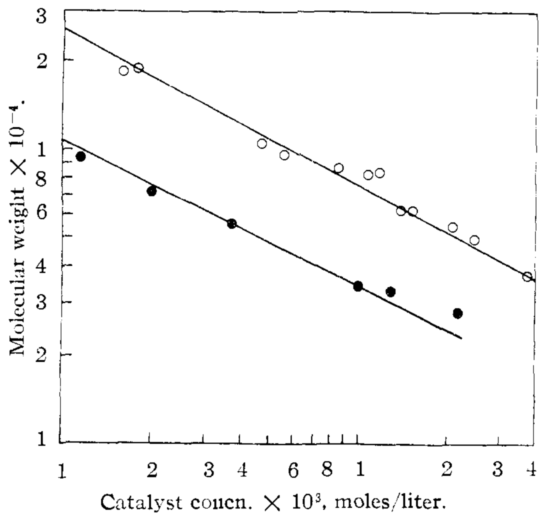

Fig. 3.—Log molecular wt. *vs.* log [Cat] for styrene polymerization: ○, initiated by *t*-butyl N-phenylperoxycarbamate at 50.7°; ●, initiated by cumyl N-phenylperoxycarbamate at 51.0°; slopes: ○, 0.51; ●, 0.49.

of Tables I and II were used to construct Fig. 4, which is a plot of $1/\bar{P}_n$ against $R_p/(M).^2$ As previously shown by Tobolsky and Johnson[8] for other initiators, linearity of this plot demonstrates the absence of transfer reaction with the *t*-butyl N-phenylperoxycarbamate over the concentration range of initiator employed.

TABLE I

POLYMERIZATION OF STYRENE WITH *t*-BUTYL N-PHENYLPEROXYCARBAMATE AT 50.7°

(Cat) × 10³, moles/liter	Conv.,[a] %	$R_p \times 10^5$, moles/l. sec.	$R'_i \times 10^8$, moles/l. sec.	f'
1.60	3.1	1.50	0.860	1.08
1.77	3.6	1.74	1.130	1.12
3.30	. .	2.88	3.16	0.84
4.68	6.0	2.04	1.46	0.95
5.60	6.9	3.34	4.26	1.34
8.73	6.9	3.36	4.04	0.93[c]
10.31	8.4	4.06	6.30	.93
10.38	8.6	4.16	6.62	.95
14.10	9.1	4.40	7.41	.92
14.95	8.8	4.28	6.95	.93[c]
20.70	9.1[b]	5.51	11.62	.99
24.71	11.5	5.58	11.90	.96[c]
36.74	15.6	7.58	22.00	.95

[a] Reaction time 5 hr. [b] Sample removed after 4 hr. [c] Temperature at 50.0 ± 0.02°.

Cumyl N-Phenylperoxycarbamate.—The decomposition of cumyl N-phenylperoxycarbamate has been studied at four temperatures: 50.7, 61.7, 74.5 and 82.0°. Figure 5 shows this to be a first-order decomposition for which the unimolecular rate constant k_d is calculated

$$k_d = 1.26 \times 10^{14} \exp(-28{,}100 \text{ cal.}/RT) \text{ sec.}^{-1} \quad (6)$$

Tables III and IV summarize the polymerization of styrene and methyl methacrylate with this initiator at 52°.

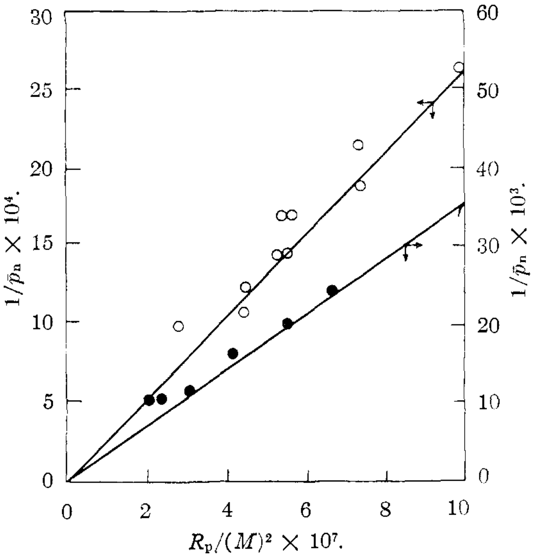

Fig. 4.—Styrene polymerization: ○, initiated by *t*-butyl N-phenylperoxycarbamate at 50.7°; ●, initiated by cumyl N-phenylperoxycarbamate at 51.0°.

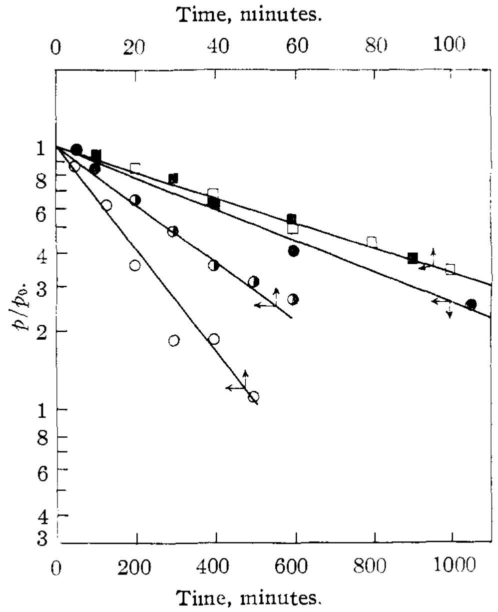

Fig. 5.—Decomposition of cumyl N-phenylperoxycarbamate in xylene at several temperatures. Initial peroxide concentration at 67.1°: □, 22.68×10^{-3}; ■, 4.00×10^{-3}; at 50.7°: ●, 5.38×10^{-3}; at 74.5°: ◑, 7.38×10^{-3}; at 82.0°: ○, 3.60×10^{-3}.

Figure 2 presents logarithmic plots of polymerization rate, R_p, against catalyst concentration for styrene and methyl methacrylate. The value of A' used for methyl methacrylate is that given by the expression (ref. 9)

$$A' = 5.02 \times 10^{-5} \exp(9.35 \text{ kcal.}/RT) \quad (7)$$

A plot of molecular weight *versus* catalyst concentration is given in Fig. 3 for polystyrene, and denotes a slope of 0.49. Figure 4 shows a plot of $1/\bar{P}_n$ against $R_p/(M)^2$ for polystyrene, as explained previously.

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(8) A. V. Tobolsky and D. H. Johnson, THIS JOURNAL, **74**, 938 (1952).

(9) A. V. Tobolsky and B. Baysal, *J. Polymer Sci.*, **11**, 471 (1953).

TABLE II

DETERMINATION OF EFFECT ON MOLECULAR WEIGHT OF VARYING CATALYST CONCENTRATION

(Cat) × 10³, moles/liter	[η]	$\overline{P}_n$	$10^4/\overline{P}_n$	$\overline{M}_n \times 10^{-4}$	$\frac{R_p}{(M)^2} \times 10^7$
1.60	1.14	1890	5.32	19.65	1.98
1.77	1.14	1890	5.37	19.65	2.28
4.68	0.77	1010	9.90	10.50	2.69
5.60	.68	935	10.70	9.72	4.40
8.73	.62	824	12.13	8.57	4.43
10.31	.54	704	14.20	8.32	5.36
10.38	.54	704	14.20	8.32	5.48
14.10	.49	597	16.75	6.21	5.80
14.95	.49	597	16.75	6.21	5.65
20.70	.45	531	18.83	5.52	7.27
24.71	.41	468	21.36	4.87	7.36
36.74	.34	362	27.60	3.76	10.00

TABLE III

POLYMERIZATION OF STYRENE WITH CUMYL N-PHENYLPEROXYCARBAMATE AT 52°

(Cat) × 10³, moles/liter	Conv.,[a] %	$R_p \times 10^6$, moles/l.-sec.	$R'_i \times 10^8$, moles/l.-sec.	f'
0.65	0.93	2.26	1.95	0.76
1.15	1.30	3.14	3.67	.74
2.00	1.70	4.11	5.92	.74
3.77	2.06	5.00	9.62	.63
10.12	3.64	8.81	27.13	.67
13.44	3.97	9.61	39.95	.64
23.45	5.22	12.66	56.20	.60

[a] Reaction time 1 hr.

TABLE IV

POLYMERIZATION OF METHYL METHACRYLATE WITH CUMYL N-PHENYLPEROXYCARBAMATE AT 52°[a]

(Cat) × 10³, moles/liter	Conv.,[a] %	$R_p \times 10^6$, moles/l.-sec.	$R'_i \times 10^8$, moles/l.-sec.	f'
1.59	3.18	16.60	5.63	0.88
5.53	5.48	28.62	16.69	.80
9.00	6.51	34.00	23.58	.66
12.06	7.60	39.67	32.11	.66
19.50	9.17	47.87	46.74	.60

[a] Reaction time 1 hr.

TABLE V

THE EFFECT ON THE MOLECULAR WEIGHT OF POLYSTYRENE OF VARYING THE CONCENTRATION OF CUMYL N-PHENYLPEROXYCARBAMATE

(Cat) × 10³, moles/liter	[η]	$\overline{P}_n$	Mol. wt.	$10^3/\overline{P}_n$	$R_p/M^2 \times 10^7$
0.65	0.965	1507	157,000	0.664	2.98
1.15	.660	897	93,300	1.115	4.14
2.00	.540	682	70,900	1.467	5.42
3.77	.450	531	55,200	1.880	6.59
10.12	.315	326	34,000	2.980	11.62
13.44	.810	319	33,200	3.220	12.67
23.45	.275	271	28,200	3.640	16.65

t-Butyl N-α-Naphthylperoxycarbamate.—Induced decomposition at peroxide concentrations as low as 10^{-4} M prevents the accurate determination of the rate constant for unimolecular decomposition.

Data on the polymerization of styrene at 29.9° and 51° are given in Table VI.

Figure 6 presents a plot of R_p *vs.* concentration of catalyst for the polymerization of styrene at the two temperatures. In Figure 7, the plot of molecular weight *vs.* concentration of catalyst clearly shows a deviation from the normal slope of 0.5.

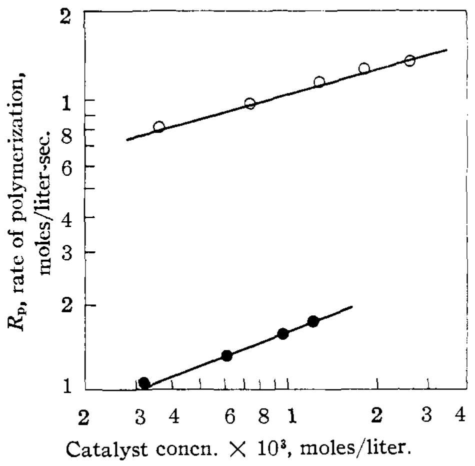

Fig. 6.—Polymerization of styrene initiated by t-butyl N-α-naphthylperoxycarbamate: ○, at 51.0°; ●, at 29.9°; slopes: ○, 0.26; ●, 0.38.

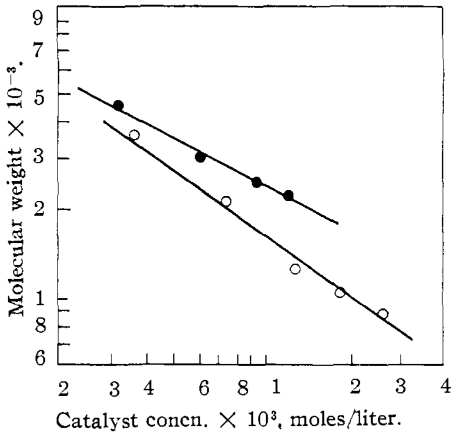

Fig. 7.—Log molecular wt. *vs.* log [Cat] for styrene polymerization initiated by t-butyl N-α-naphthylperoxycarbamate: ○, at 51.0°; ●, 29.9°; slopes: ○, 0.62; ●, 0.56.

TABLE VI

POLYMERIZATION OF STYRENE WITH t-BUTYL N-α-NAPHTHYLPEROXYCARBAMATE AT 29.9 AND 51.0°

Temp., °C.	(Cat) × 10³, moles/l.	Conv.,[a] %	R_o, moles/l.-sec.	R'_i, moles/l.-sec.	$f'k_d$
51.0	3.63	3.28	7.94×10^{-5}	2.07×10^{-7}	2.85×10^{-5}
	7.41	4.06	9.82	3.17	2.14
	12.74	4.74	11.47	4.34	1.70
	18.00	5.16	12.50	4.80	1.33
	25.40	5.48	13.26	5.79	1.14
29.9	3.17	0.418	10.11×10^{-6}	13.27×10^{-9}	2.09×10^{-6}
	6.14	.550	13.31	23.14	1.99
	9.38	.646	15.63	31.73	1.69
	12.03	.712	17.23	38.55	1.40

[a] Reaction time 1 hr.

Table VII contains the data showing the effect of catalyst concentration on molecular weight, while a plot of $1/P_n$ *vs.* R_p is presented in Fig. 8.

In order to establish whether the initial conversion followed a linear path with time, the conversion was measured, at constant catalyst, varying the time.

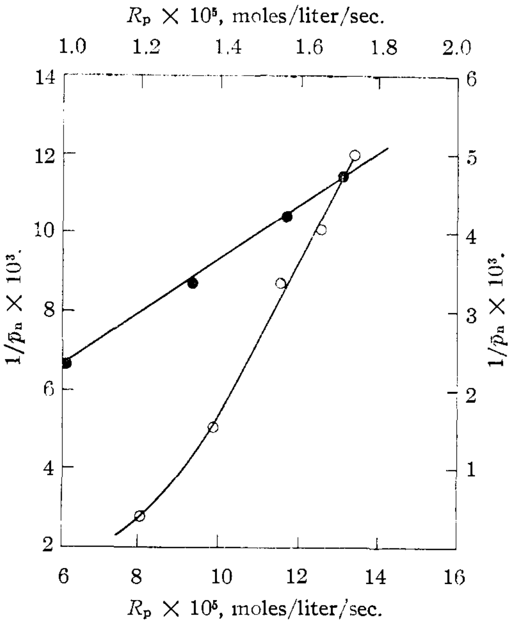

Fig. 8.—Styrene polymerization initiated by *t*-butyl N-α-naphthylperoxycarbamate; ○, 51.0°; ●, 29.9°.

Discussion

Although much work on the initiation of polymerization with symmetrical peroxides has been done, initiation with peroxides capable of forming dissimilar free radicals has been studied only with alkyl perbenzoates,[10] *t*-butyl hydroperoxide[11] and cumyl hydroperoxide.[8]

For the peroxycarbamates studied, the decomposition products appear to be carbon dioxide, an arylimino free radical and an alkoxy or aralkoxy free radical.

$$\mathrm{ArNH\overset{\overset{\displaystyle O}{\|}}{C}OOR} \longrightarrow \mathrm{ArNH\cdot} + \mathrm{CO_2} + \mathrm{RO\cdot}$$

This is supported by the fact that hydrazobenzene and azobenzene are the main products. This is also in agreement with work done on related compounds.[12]

Bell, Rust and Vaughan[13] have shown that both the *t*-butoxy radical and its decomposition product, the methyl radical, can initiate polymerization. Similar studies[8,14] on the products of the decomposition of cumene hydroperoxide have shown that cumyl (or methyl radicals derived from the cumyl) radical can initiate polymerization. The fate of the RO· radical is therefore well established whether it be cumyloxy or *t*-butoxy.

TABLE VII

THE EFFECT ON THE MOLECULAR WEIGHT OF POLYSTYRENE OF VARYING THE CONCENTRATION OF *t*-BUTYL N-α-NAPHTHYLPEROXYCARBAMATE

Temp., °C.	(Cat) × 10^{-3}, moles/l.	[η]	$\bar{P}_n$	$10^3/\bar{P}_n$	Mol. wt.
51.0	3.63	0.336	356	2.81	37,000
	7.41	.222	202	4.95	21,000
	12.74	.153	121	8.26	12,600
	18.00	.130	100	10.00	10,400
	25.40	.117	84	11.90	8,730
29.9	3.17	.390	437	2.29	45,500
	6.14	.295	298	3.36	31,000
	9.38	.250	237	4.22	24,700
	12.03	.230	212	4.72	22,200

The formation of two dissimilar free radicals presents, in this case, two alternatives: (a) both radicals will initiate, or (b) one radical will initiate and one will not whereupon the latter may terminate with itself or other radicals in the system. In deciding this, the resonance stability of the primary amino radical ArNH· is an important consideration. From the calculated values of *f'* it was shown that the anilino radical can initiate the polymerization of styrene and methyl methacrylate with high efficiency, whereas the α-naphthylimino radical appears to be of low or variable efficiency. From the data presented, it is clear that *t*-butyl and cumyl N-phenylperoxycarbamates obey those equations which are commonly used for free radical polymerization, without appreciable chain transfer or induced decomposition. On the other hand, a large amount of induced decomposition and chain transfer with *t*-butyl N-α-naphthylperoxycarbamate is indicated by the decrease in efficiency (*f'*) with increased catalyst concentration and the effect of catalyst concentration on molecular weight.

For styrene polymerization initiated by *t*-butyl N-α-naphthylperoxycarbamate the $\overline{DP}$ calculated from the rate data varies greatly from the $\overline{DP}$ arrived at from the viscosity equation.[7] If one recalculates R'_i from R_p and the degree of polymerization as established by viscosity measurements, the large decrease in $f'k_d$ disappears and that expression becomes almost constant. It seems likely, therefore, that variation from normal kinetics is due almost entirely to chain transfer with the catalyst.

It seems likely that the greater ease of formation of the α-naphthylimino radical (as compared to the anilino radical) and its decreased reactivity toward styrene stems from the greater resonance stabilization of the radical.

No accurate estimate can be offered now as to the extent to which the rate of decomposition of the peroxycarbamates is influenced by resonance stabilization of the free radicals formed.

BROOKLYN 1, N. Y.

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[10] A. T. Blomquist and A. F. Ferris, THIS JOURNAL, **73**, 3214 (1951).

[11] R. N. Haward and W. Simpson, *Trans. Faraday Soc.*, **47**, 212 (1951).

[12] H. Esser, K. Rastadter and G. Reuter, *Chem. Ber.*, **89**, 685 (1965).

[13] E. R. Bell, F. F. Rust and W. E. Vaughan, THIS JOURNAL, **72**, 337 (1950).

[14] B. Baysal and A. V. Tobolsky, *J. Polymer Sci.*, **8**, 529 (1952).