molecule. (4) The *cis*-keto form is produced in the thermal back-reaction from the *trans*-keto form as

$$trans\text{-keto} \xrightarrow{\Delta} cis\text{-keto} \xrightarrow{\Delta} \text{enol}$$

(5) The emission spectrum of the enol is actually that of a species closely resembling the *cis*-keto form which is designated "enol."

Several investigators[3-5,8] have postulated the formation of a quinoid (keto) isomer by irradiation of various anils in both solution and crystal. However, in solution the geometric isomer involved was not defined,[8] possibly incorrectly defined,[5] or not definitively considered.[3,4] In the crystal, both a *cis*- and *trans*-keto form were postulated and were associated separately with thermochromic or photochromic behavior.[3,9] In the case of the Russian work,[5] the emission spectra indicate the possibility of the presence of the *trans*-keto form; however, some of the bands existing for the colored species are residual from those of the uncolored species, making interpretation difficult. Emission from the *cis*-keto form is considerably more intense than that from the *trans*-keto form. If any hydrogen-bonding solvents were initially present, the *cis*-keto emission would be present before and after irradiation of the anil. In any event, the colored species was indicated to be the *cis*-keto rather than the *trans*-keto form.

The most extensive investigations have been those of Cohen, *et al.*[3,4,9] In a general sense, the results of this investigation and those of Cohen, *et al.*, are compatible. The one notable exception is that nitrosalicylidene anils are not photochromic, which is contradictory to the generality they give. With the knowledge of the present investigation, it is possible to interpret some of their results. The weak absorption they note in the 424–500-mμ region for some anils in a strongly hydrogen-bonding solvent or at low temperature can now be associated with the formation of the *cis*-keto form. Further, the broader absorption in the 425–580-mμ region resulting from irradiation of the anils can be assigned as arising from the photochemically produced *trans*-keto form. Also, the fact that only partial photoerasure occurs in some cases[4] can be explained on the basis of the presence of both *cis*- and *trans*-keto forms and the inability to photoconvert the *cis*-keto form to the enol form.

Further investigation of the hydroxynaphthaldehyde and -salicylaldehyde anils is in progress.

(9) M. D. Cohen, G. M. J. Schmidt, and S. Flavian, *J. Chem. Soc.*, 2041 (1964).

Photosensitized Chain Reactions in Alkaline Solutions of Nitrous Oxide in 2-Propanol

Warren V. Sherman[1]

Contribution from the Soreq Nuclear Research Centre, Yavne, Israel.

Received October 27, 1966

Abstract: Solutions of di-*t*-butyl peroxide (DTBP) in 2-propanol have been photolyzed under anaerobic conditions with a high-pressure mercury lamp. In the absence of any other solute, DTBP was consumed and acetone formed at identical rates. The addition of potassium hydroxide considerably increased both rates, and a base-catalyzed chain reaction is indicated. Large yields of nitrogen, methane, acetone, and potassium acetate were produced in the photolysis of alkaline solutions containing both DTBP and nitrous oxide. The magnitude of the product yields suggests a chain reaction involving nitrous oxide. The reaction was retarded and inhibited by small concentrations of nitrobenzene, benzophenone, and carbon tetrachloride, but relatively unaffected by benzene and acetone. In all experiments the ratio of yields of nitrogen:methane remained constant (14 ± 2). The dependence of the yields on the concentrations of potassium hydroxide and nitrous oxide closely resembled that found in the γ radiolysis of alkaline solutions of nitrous oxide in 2-propanol in the absence of DTBP. It is concluded that DTBP acts both as a photosensitizer and a chain terminator in the light-induced reaction, and apart from the modes of initiation and termination the reaction mechanisms are identical. Nitrogen was also formed in the photolysis of alkaline solutions containing benzophenone and nitrous oxide, but in yields which were lower than observed in the DTBP-sensitized reaction. Methane was produced in addition to nitrogen only in the presence of low initial concentrations of benzophenone.

It has been shown that the cobalt-60 radiolytic decomposition of nitrous oxide in alkaline 2-propanol solutions involves a chain reaction.[2] In a more detailed study[3] it is suggested that the propagation steps for the formation of nitrogen involve the transfer of an electron from the ketyl radical anion I to nitrous oxide.

$$\underset{\text{I}}{(CH_3)_2\dot{C}O^-} + N_2O \longrightarrow (CH_3)_2CO + N_2O^- \quad (1)$$

$$N_2O^- \longrightarrow N_2 + O^- \quad (2)$$

$$O^-(\text{or } N_2O^-) + (CH_3)_2CHOH \longrightarrow OH^-(\text{or } N_2 + OH^-) + \underset{\text{II}}{(CH_3)_2\dot{C}OH} \quad (3)$$

$$\text{II} + (CH_3)_2CHO^- \longrightarrow \text{I} + (CH_3)_2CHOH \quad (4)$$

If the above mechanism is in fact correct, it should be possible to initiate the same chain reaction in the ab-

[1] The Radiation Laboratory, University of Notre Dame, Notre Dame, Ind.

[2] W. V. Sherman, *Chem. Commun.*, 250 (1966).

[3] W. V. Sherman, *J. Phys. Chem.*, in press.

sence of ionizing radiation by introducing into an alkaline solution of nitrous oxide in 2-propanol any reactive species capable of abstracting the carbinol hydrogen atom of the solvent to yield the radical anion I.

Di-*t*-butyl peroxide undergoes homolytic scission when exposed to ultraviolet light to give two *t*-butoxy radicals per molecule.[4] These radicals abstract the carbinol hydrogen of 2-butanol when generated in this solvent,[5] and hence the photolysis of 2-propanol solutions containing DTBP and a base would appear to be a suitable method for producing the solvent radical II and subsequently the radical anion I. Similarly, the light-induced reduction of benzophenone to benzhydrol in alkaline 2-propanol solutions involves I as an intermediate.[6,7] The photolysis of alkaline solutions of these two potential photosensitizers was therefore studied in the presence of nitrous oxide in order to ascertain whether a chain reaction similar to that initiated by Co^{60} γ rays would be observed.

Experimental Section

2-Propanol (Eastman Spectrograde) and nitrous oxide (Matheson) were purified as described previously.[8] DTBP (Fluka) was used as received; no impurity was detectable by gas chromatography. Benzophenone (Fluka) was recrystallized from aqueous ethanol to constant melting point (47°). All other solutes were of reagent grade and used as received.

Standard 2-propanol solutions were prepared, and 2-ml aliquots were placed in Pyrex reaction vessels consisting of a 20-mm diameter tube sealed at one end and fitted with a break-seal and a standard-taper joint at the other. The solutions were then thoroughly degassed; nitrous oxide was added, and then the vessels were sealed in the manner described previously.[8] They were then irradiated. The ultraviolet source was a high-pressure mercury lamp (Quarzlampen Gesellschaft, Hanau, Type PL321). It was mounted vertically on an optical bench so that the radiation intensity incident on the sample could be varied by altering the lamp–reaction vessel distance. The samples were fan-cooled, and it was found that they remained at room temperature (25–30°) at the lamp distances used in the experiments (10 and 30 cm). After photolysis the samples were attached to a vacuum line and the gaseous products removed by means of a Toepler pump and analyzed by gas chromatography as described previously.[3,8] Acetone and DTBP were analyzed by gas chromatography (F & M Model 810) using a column of 10% Carbowax 20M on Chromosorb S. Potassium acetate was identified as indicated previously.[3] The disappearance of benzophenone was followed spectrophotometrically by the decrease in its ultraviolet absorption band at 333 mμ.[7]

Results

1. Photolysis of Neutral and Alkaline Solutions of DTBP. In any given experiment in this series (Table I) DTBP disappeared and acetone was formed at approximately equal rates. With the alkaline solutions the rates were dependent on the intensity of illumination (distance from the lamp) and the initial concentration of DTBP, but independent of the period of illumination. For solutions initially containing 5×10^{-2} M DTBP, the presence of potassium hydroxide significantly increased the reaction rate.

2. Time and Illumination-Intensity Effects in the Photolysis of Solutions Containing DTBP, Potassium Hydroxide, and Nitrous Oxide. Nitrogen and methane were produced in addition to acetone in the photolysis of alkaline solutions containing DTBP and nitrous oxide. Potassium acetate was also identified in experiments in which high yields of gaseous products were observed but not analyzed quantitatively.[3]

Table I. Photolysis of Neutral and Alkaline Solutions of DTBP

$[KOH]_0$, mM	$[DTBP]_0$, mM	Lamp distance, cm	Illumination time, min	Product, −DTBP	mM min^{-1} Acetone
...	50	10	30	...	0.039
...	50	10	120	0.039	0.041
...	50	10	240	0.036	0.036
50	5	10	50	0.019	0.021
50	5	10	100	0.022	0.020
50	5	30	200	0.0043	0.0040
50	50	10	10	...	0.56
50	50	10	20	0.55	0.54
50	50	10	30	0.63	0.59
50	50	10	50	0.56	0.57
50	50	30	60	0.20	0.18
50	50	30	180	0.20	0.17
50	500	10	20	5.3	5.3
50	500	10	60	5.4	5.1
50	500	30	60	...	1.3
50	500	30	150	1.3	1.1

The dependence of reaction rate on the period of illumination was studied at three initial DTBP concentrations (Table II). In all cases the rate of production of nitrogen, methane, and acetone remained approximately constant with time up to about 50% conversion of nitrous oxide to nitrogen. For periods in excess of this, the rates decreased progressively with time. On prolonged illumination 100% conversion of nitrous oxide to nitrogen was noted. No change in the concentration of DTBP was distinguishable after illumination periods corresponding to less than 50% nitrous oxide conversion. However, decreases in DTBP concentration could be noted after prolonged illumination, the rate remaining approximately constant with time.

For a given illumination intensity, the reaction rates were found to decrease with increasing initial concentration of DTBP.

The effect of decreasing the illumination intensity to one-ninth (by increasing the lamp–sample distance from 10 to 30 cm) was studied with solutions initially containing 5×10^{-3} and 5×10^{-2} M DTBP (Table II). Although decreases in absolute rates were observed, the yields per photon of light to which the reaction vessels were exposed increased approximately threefold at both concentrations.

3. Concentration Effects in the Photolysis of Solutions Containing DTBP, Potassium Hydroxide, and Nitrous Oxide. With a constant initial concentration of DTBP (5×10^{-2} M) and nitrous oxide (2×10^{-1} M), the effect of the variation of the concentration of potassium hydroxide was studied (Figure 1). No gaseous products were detectable in samples containing 1×10^{-3} M or less potassium hydroxide. At higher concentrations, nitrogen and methane were identified as products together with an increased yield of acetone. The yields increased progressively with increasing potassium hydroxide concentration up to about 2×10^{-2} M and then became relatively insensitive to further increases.

At constant alkalinity ([KOH] = 5×10^{-2} M), the yields of nitrogen, methane, and acetone were observed

---

[4] L. M. Dorfman and Z. W. Salsburg, *J. Am. Chem. Soc.*, **73**, 255 (1951).

[5] E. S. Huyser and D. C. Neckers, *ibid.*, **85**, 3641 (1963).

[6] A. Beckett and G. Porter, *Trans. Faraday Soc.*, **59**, 2038 (1963).

[7] S. G. Cohen and W. V. Sherman, *J. Am. Chem. Soc.*, **85**, 1642 (1963).

[8] W. V. Sherman, *J. Phys. Chem.*, **70**, 667 (1966).

Table II. Photolysis of Alkaline Solutions of DTBP and Nitrous Oxide. Product Yields as a Function of Illumination Time and Intensity[a]

[DTBP], mM	Lamp distance, cm	Illumination time, min	Products, mM min^{-1}			
			−DTBP	N_2	CH_4	Acetone
. . .	10	10	. . .	0	0	0
5	10	1	. . .	26	1.8	18
5	10	2	. . .	26	1.8	18
5	10	3	. . .	25	1.5	17
5	10	4	. . .	20	1.2	15
5	10	30	0.073	6.7	0.41	4.5
5	30	10	. . .	6.9	0.50	5.0
50	10	0.5	. . .	18	1.2	17
50	10	1	. . .	17	1.1	16
50	10	2	. . .	18	1.2	15
50	10	4	. . .	18	1.1	12
50	10	6	. . .	15	1.0	11
50	10	15	0.73	10	0.70	8.7
50	10	20	0.85	. . .	. . .	6.9
50	10	30	0.83	6.5	0.43	5.5
50	30	10	. . .	5.0	0.31	3.6
50	30	20	. . .	6.4	0.43	5.2
50	30	30	0.33	5.7	0.36	4.1
50	30	60	0.30	3.3	0.20	2.6
50	30	120	0.27	1.7	0.11	1.5
500	10	3	. . .	6.0	0.35	6.7
500	10	5	. . .	8.1	0.51	8.0
500	10	7	. . .	12	0.72	11
500	10	9	. . .	12	0.80	13
500	10	30	3.1	6.3	0.45	8.7

[a] [KOH] = 5×10^{-2} M, [N_2O] = 2×10^{-1} M.

to increase linearly with the initial concentration of nitrous oxide (Figure 2).

4. **Solute Effects in the Photolysis of Alkaline Solutions of DTBP and Nitrous Oxide.** The solutes studied and the results are listed in Table III. Nitrobenzene, benzophenone, and carbon tetrachloride retarded and inhibited product formation, while the presence of acetone and benzene had little effect on the yields. Inhibition by carbon tetrachloride was accompanied by the formation of carbon monoxide, a new product.

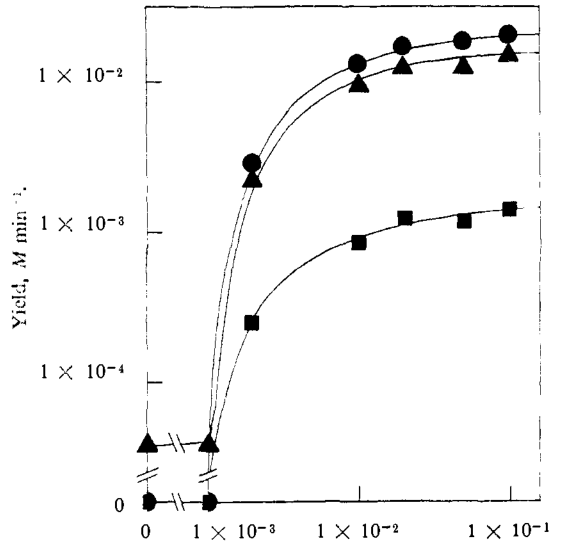


Figure 1. Photolysis of alkaline 2-propanol solutions containing DTBP (5×10^{-2} M) and nitrous oxide (2×10^{-1} M). Product yields as a function of potassium hydroxide concentration: ●, N_2; ■, CH_4; ▲, acetone.

In order to distinguish whether simple masking was contributing to the observed effects, the extinction coefficients of DTBP and the solutes were determined (Table IV) at wavelengths above the cut-off of the glass used in the reaction vessels (290 mμ).

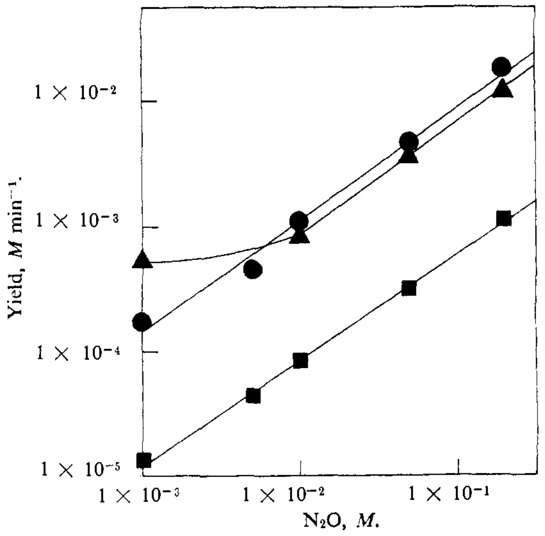


Figure 2. Photolysis of alkaline 2-propanol solutions containing DTBP (5×10^{-2} M) and nitrous oxide. Product yields as a function of nitrous oxide concentration: ●, N_2; ■, CH_4; ▲, acetone.

5. **Photolysis of Alkaline Solutions Containing Benzophenone and Nitrous Oxide.** With the initial concentration of potassium hydroxide and nitrous oxide kept constant, product yields were determined as a function of the initial benzophenone concentration (Table V). Nitrogen yields of the same order of magnitude were

Table III. Photolysis of Alkaline Solutions of DTBP and Nitrous Oxide. Effect of Solutes on Product Yields[a]

Solute	Concn, M	Illumination time, min	Products, mM min^{-1} N$_2$	CH$_4$	Acetone
Nitrobenzene	1×10^{-5}	3	11	0.84	8.2
	1×10^{-5}	6	12	0.81	9.0
	1×10^{-3}	3	0[b]	0[b]	...
Benzophenone	5×10^{-5}	3	0.69	0.045	...
Benzene	1×10^{-1}	3	17	1.1	15
Acetone	1×10^{-1}	3	20	1.3	...
Carbon tetrachloride	5×10^{-3}	3	0.63	0.042	2.6
	5×10^{-2}	3	0[c]	0[c]	...

[a] [DTBP] and [KOH] = 5×10^{-2} M, [N$_2$O] = 2×10^{-1} M, lamp distance, 10 cm. [b] Total gaseous products $<1 \times 10^{-6}$ M. [c] Carbon monoxide identified as the sole gaseous product. The yield was 0.11 mM min^{-1}.

Table IV. Extinction Coefficients[a] of Solutes Listed in Table III

Solute	ϵ_{290}	ϵ_{300}	ϵ_{310}	ϵ_{320}	ϵ_{340}
DTBP	3.8	2.8	1.9	1.2	3.6×10^{-1}
Carbon tetrachloride	0	0	0	0	0
Acetone	5.1	2.7	1.0	1.8×10^{-1}	0
Benzene	0	0	0	0	0
Nitrobenzene	4.0×10^{3}	1.7×10^{3}	4.8×10^{2}	2.7×10^{2}	1.8×10^{2}
Benzophenone	3.0×10^{3}	8.5×10^{2}	1.2×10^{2}	1.3×10^{2}	1.5×10^{2}

[a] Measured in 2-propanol containing 5×10^{-2} M potassium hydroxide.

Table V. Photolysis of Alkaline Solutions of Benzophenone and Nitrous Oxide. Product Yields as a Function of Benzophenone Concentration[a]

[Benzophenone]$_0$, M	Illumination time, min	Products, mM min^{-1} N$_2$	CH$_4$	−Benzophenone
5×10^{-2}	30	0.21	0	0.50
5×10^{-3}	3	0.32	0	0.90
5×10^{-4}	3	0.17	6.6×10^{-4}	...
5×10^{-5}	3	0.15	4.4×10^{-2}	...

[a] [KOH] = 5×10^{-2} M, [N$_2$O] = 2×10^{-1} M, lamp distance, 10 cm.

noted at all four concentrations. At high benzophenone concentration no methane was detectable, but significant yields were noted at the two lower concentrations.

A preliminary study of the effect of the variation of the initial concentrations of potassium hydroxide and nitrous oxide was made with solutions initially containing 5×10^{-5} M benzophenone. With the initial concentration of nitrous oxide kept constant, the shape of the nitrogen or methane yield *vs.* [KOH] plot was similar to that shown in Figure 1. No nitrogen was detectable with initial potassium hydroxide concentrations of 1×10^{-3} M or less. At a constant potassium hydroxide concentration the yields increased in proportion to the initial concentration of nitrous oxide.

Discussion

The disappearance of DTBP and the formation of acetone at equal rates in the photolysis of neutral solutions of 5×10^{-2} M DTBP is consistent with reactions

$$\text{DTBP} \xrightarrow{h\nu} 2(\text{CH}_3)_3\text{CO}\cdot \tag{5}$$

$$(\text{CH}_3)_3\text{CO}\cdot + (\text{CH}_3)_2\text{CHOH} \longrightarrow (\text{CH}_3)_3\text{COH} + \text{II} \tag{6}$$

$$\text{II} + \text{II} \longrightarrow (\text{CH}_3)_2\text{CHOH} + (\text{CH}_3)_2\text{CO} \qquad (7)^{9}$$

5–7. No significant alteration was observable in the absorbance above 290 mμ of solutions of DTBP on the addition of potassium hydroxide. Hence the enhanced rates of DTBP disappearance and acetone formation observed in the presence of potassium hydroxide cannot be attributed to an increase in the light absorbed by the solution. It may be reasonably assumed therefore that the absorption of ultraviolet light by DTBP in the presence of potassium hydroxide results in the same initial yield of *t*-butoxy radicals, and the observed catalysis by potassium hydroxide involves subsequent reactions. The large increase in rates (approximately 15-fold) indicates that a chain reaction was operative. One that may be readily written involves reactions 8 and 9.[10] The pK_a of a radical is invariably greater

$$\text{II} + (\text{CH}_3)_2\text{CHO}^- \rightleftharpoons \text{I} + (\text{CH}_3)_2\text{CHOH} \tag{8}$$

$$\text{I} + \text{DTBP} \longrightarrow (\text{CH}_3)_2\text{CO} + (\text{CH}_3)_3\text{CO}\cdot + (\text{CH}_3)_3\text{CO}\cdot^- \tag{9}$$

than that of the compound from which it has been derived by the removal of a hydrogen atom. Hence, in the equilibrium 8 the left-to-right reaction is much faster than the back-reaction. A photochemical chain reaction terminated by a reaction of the chain carrier which is second-order exhibits an increasing kinetic chain length with decreasing light intensity.[11] At all three initial DTBP concentrations (5×10^{-3}, 5×10^{-2}, and 5×10^{-1} M, see Table I), decreasing the light intensity to one-ninth by increasing the lamp–sample separation to 30 cm resulted in rates which were significantly greater than one-ninth of the rates at 10 cm. This intensity effect is consistent with the above chain mechanism involving a second-order termination step, such as[12]

$$\text{I} + \text{I} \xrightarrow{(\text{CH}_3)_2\text{CHOH}} (\text{CH}_3)_2\text{CO} + 2(\text{CH}_3)_2\text{CHO}^- \tag{10}$$

---

(9) Since (a) a good balance between the disappearance of DTBP and the yield of acetone was obtained, and (b) no pinacol was detectable, the combination of two radicals II would appear to be unimportant. However, E. S. Huyser and C. J. Bredeweg, *J. Am. Chem. Soc.*, 86, 2401 (1964), have suggested that acetone may be formed by a disproportionation reaction between a *t*-butoxy radical and the alcohol-derived radical II.

(10) Reaction 9 is analogous to the process proposed by M. F. Hawthorne and G. S. Hammond, *J. Am. Chem. Soc.*, 77, 2549 (1955), for the decomposition of a hydroperoxide in alkaline ethanolic solution: $\text{R}_3\text{C}\cdot^- + \text{R}_3\text{COOH} \rightarrow \text{R}_3\text{C}\cdot + \text{R}_3\text{CO}\cdot + \text{OH}^-$, where R = *p*-NO$_2C_6H_4$.

(11) F. S. Dainton, "Chain Reactions," Methuen & Co., Ltd., London, 1956, p 80.

(12) This disproportionation reaction between two anions involving a simultaneous proton transfer from the solvent is analogous to that proposed in ref 7 for the benzophenone ketyl radical anion.

Alkaline solutions of nitrous oxide in 2-propanol are transparent to light which is transmitted by Pyrex glass. The photolysis of such a solution contained in a Pyrex ampoule led to no detectable reaction. Hence, the observed reaction in the presence of DTBP is in accord with the latter participating as a photoinitiator. The relatively high rates of formation of nitrogen and methane compared with the rate of disappearance of DTBP indicate that a chain reaction is involved. The light-induced reaction closely parallels the γ radiolysis of alkaline solutions of nitrous oxide (containing no DTBP)[2,3] in four salient features: (i) the profile of the reaction rate *vs.* potassium hydroxide concentration plot (Figure 1) (the onset of the chain reaction occurring at a potassium hydroxide concentration slightly in excess of 1×10^{-3} M in both systems, and then the reaction rate leveling off above 2×10^{-2} M); (ii) the linear dependence of the yields of the chain products on the concentration of nitrous oxide (Figure 2); (iii) the ratio of the yields of nitrogen to methane in any given experiment remaining constant at 14 ± 2; (iv) yields of nitrogen and acetone of the same order of magnitude, with the latter consistently 10–30% lower than the former.

The relative insensitivity of the rates of product formation to the concentration of potassium hydroxide when the latter exceeds about 2×10^{-2} M indicates that, provided sufficient potassium hydroxide is present, it does not take part in a rate-determining step. The proportionality between product yields and nitrous oxide concentration is consistent with the latter participating in a rate-determining, first-order propagation step (reaction 1). The dependence of the yields on the initial concentration of DTBP (Table II) appears at first to be somewhat anomalous since we have a situation where the reaction rates decreased as the concentration of the proposed photoinitiator increased. The simplest explanation for this phenomenom is that DTBP acts as a chain terminator as well as an initiator. (However, the possibility cannot be excluded that an undetected impurity in DTBP was responsible for this effect.) Support for this proposal is derived from the observation that the rate of disappearance of DTBP increased in the presence of nitrous oxide.

The rate of initiation of the DTBP-initiated chain reaction may be equated with the rate of formation of *t*-butoxy radicals, the latter being equal to twice the rate of disappearance of DTBP in neutral solution containing no nitrous oxide. The "kinetic chain lengths" (arbitrarily defined as the product yield divided by the yield of *t*-butoxy radicals produced in the absence of potassium hydroxide and nitrous oxide) are calculated in Table VI for solutions initially containing 2×10^{-1} M nitrous oxide and various initial concentrations of DTBP. It may be observed that variation of the intensity of illumination has little effect on the kinetic chain length. This is consistent with a reaction which is first-order with respect to the chain carrier being of major importance in the termination of the chain and is in accord with the conclusion reached in the preceding paragraph.

Table VI. Photolysis of Alkaline Solutions of DTBP and Nitrous Oxide. Dependence of the Kinetic Chain Length on DTBP Concentration and Illumination Intensity[a]

$[\mathrm{DTBP}]_0$, M	Lamp distance, cm	Kinetic chain length[b] N_2	CH_4	Acetone
5×10^{-3}	10	6.5×10^{2}	4.5×10^{1}	4.5×10^{2}
5×10^{-3}	30	7.9×10^{2}	4.7×10^{1}	5.2×10^{2}
5×10^{-2}	10	1.5×10^{1}	9.2×10^{-1}	1.3×10^{1}
5×10^{-2}	30	1.6×10^{1}	1.0	1.2×10^{1}
5×10^{-1}	10	1.1	6.5×10^{-2}	9.0×10^{-1}

[a] $[\mathrm{KOH}] = 5 \times 10^{-2}$ M, $[\mathrm{N_2O}] = 2 \times 10^{-1}$ M. [b] As defined in the text.

Kinetic chain lengths considerably in excess of those calculated in Table VI were noted in the γ-ray-induced reaction.[3] It was also concluded that the major termination process was a second-order reaction. A further difference between the two systems is that product formation continued for a considerable time after the removal of the reaction mixture from the radiation source,[3] whereas there was no post-irradiation effect observable with the DTBP-initiated reaction. All these observations are consistent with DTBP acting as a chain terminator. The fact that the addition of DTBP was found to retard the γ-ray reaction[13] adds weight to this argument.

In the γ-ray reaction, the presence of nitrobenzene, benzophenone, and carbon tetrachloride reduced or inhibited the yields of the chain products, while benzene had little effect.[2,3] The same effects were found in the DTBP-photoinitiated reaction (Table III). Since nitrobenzene and benzophenone absorb strongly in the same region as DTBP, it is necessary to confirm that the observed effects were not due simply to masking of the light. From extinction coefficient measurements (Table IV), in a solution containing 5×10^{-2} M DTBP and 5×10^{-5} M benzophenone, the latter would be expected to mask not more than 20% of the light previously absorbed by DTBP when benzophenone is absent. Hence the retardation of the nitrogen and methane yields to less than 4% of the normal rate cannot be attributed to masking. Similarly, the masking effect due to the presence of 1×10^{-5} M nitrobenzene should not decrease the reaction rate by more than 17%. The observed 40% decrease is significantly in excess of this. The effect of carbon tetrachloride, which is completely transparent in the region of interest, confirms that the solute effects involve processes subsequent to the initial absorption of the light by DTBP. In view of the high reactivity of the solvent toward free radicals, it is extremely unlikely that the low concentrations of solutes used could effectively compete for the *t*-butoxy radicals. The inability of benzene and acetone, both of which are reactive to radicals, to decrease the yields of the chain products supports this contention. It was suggested previously[3] that retardation and inhibition was brought about by reaction between the solute and a chain carrier competing successfully with one of the propagation steps of the chain. Since inhibition was invariably observed with solutes which are good electron acceptors, it was concluded that the mechanism of inhibition involved competition between the inhibitor, S, and nitrous oxide for the electron of the radical anion I (reaction 11).[14] Only in the case of acetone is the

$$\mathrm{I} + \mathrm{S} \longrightarrow (\mathrm{CH_3})_2\mathrm{CO} + \mathrm{S}^- \qquad (11)$$

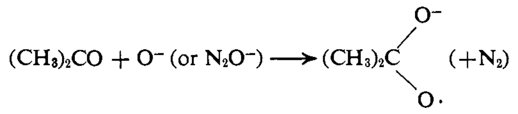
---

[13] A previously unpublished result. While the presence of DTBP significantly decreased the yields of the chain products, it was considerably less efficient than nitrobenzene or benzophenone.

solute effect different from that observed in the γ-ray reaction. Electron transfer from I to acetone leads only to a change of identity and would therefore not be expected to be a chain-terminating process. No decreases in yields were in fact observed in the presence of a large excess of acetone in the present work. The inhibition observed in the γ-ray reaction is not readily explicable in terms of the proposed chain mechanism, but a possible rationalization of this anomalous behavior is given elsewhere.[3]

Complete inhibition of the γ-ray reaction brought about by nitrobenzene and benzophenone was accompanied by the formation of a previously unobserved product, carbon monoxide.[3] No carbon monoxide was detectable in the DTBP-photoinitiated reaction in the presence of these solutes. A possible explanation is that the concentration required to inhibit completely the formation of nitrogen and methane would result in essentially all the light being absorbed by these solutes and none getting through to DTBP. However, it is interesting to note that in the case of complete inhibition by carbon tetrachloride, a significant yield of carbon monoxide was observed. A mechanism for the formation of carbon monoxide is not readily formulated.

The constancy of the ratio of the yields of nitrogen to methane is consistent with these two products resulting from a common precursor, the formation of methane constituting a side reaction of the main chain. The oxygen radical anion (formed *via* reactions 1 and 2) is initially in close proximity to an acetone molecule since N_2O^- is short-lived.[15] Reactions such as 12–14 may therefore be probable and would also account for the observed formation of potassium acetate.



$$(CH_3)_2CO + O^- \text{ (or } N_2O^-) \longrightarrow (CH_3)_2C\begin{matrix} \diagup O^- \\ \diagdown O\cdot \end{matrix} \quad (+N_2) \qquad (12)$$

III

$$\text{III} \longrightarrow CH_3\cdot + CH_3CO_2^- \qquad (13)$$

$$CH_3\cdot + (CH_3)_2CHOH \longrightarrow CH_4 + \text{II} \qquad (14)$$

The formation of nitrogen in the photolysis of alkaline solutions containing benzophenone and nitrous oxide is consistent with radical anion I, an intermediate in the photoreduction of benzophenone in alkaline 2-propanol,[6,7] bringing about the decomposition of nitrous oxide (reaction 1). The parallel dependence of the nitrogen yields on the concentrations of nitrous oxide and potassium hydroxide in the benzophenone- and DTBP-initiated reactions supports the conclusion that essentially the same chain reaction is involved in both systems. The fact that the kinetic chain length for a given initiator concentration is smaller in the benzophenone reaction than in the DTBP reaction would appear to indicate that benzophenone also acts as a chain terminator, its efficiency being greater than that of DTBP. The observation that benzophenone is more effective than DTBP in retarding the γ-ray reaction[13] supports this suggestion, as does the result (Table III) that a small concentration of benzophenone will retard the DTBP-photoinitiated chain.

Acknowledgments. The experimental work was carried out during the tenure of an Israel Atomic Energy Commission Fellowship. The author wishes to thank Dr. Arie Rajbenbach for many helpful discussions.

---

(14) The facility with which nitroaromatics and diaryl ketones undergo electron-transfer reactions with organic anions has been documented by G. A. Russell, E. G. Janzen, and E. T. Strom, *J. Am. Chem. Soc.*, **86**, 1807 (1964).

(15) F. S. Dainton, *Radiation Res., Suppl.*, **4**, 71 (1964).

The Initial-State Contribution to the Activation Volume for Benzyl Chloride Solvolysis

H. S. Golinkin, Ikchoon Lee, and J. B. Hyne

Contribution from the Department of Chemistry, The University of Calgary, Calgary, Alberta, Canada.

Received October 19, 1966

Abstract: The first-order rate constants for the solvolysis of benzyl chloride in aqueous methyl, isopropyl, and *t*-butyl alcohols are reported at 50.25° and various pressures up to 4000 atm. The activation volume is calculated from these data and is seen to exhibit extremum behavior with solvent composition in each of the systems studied. The partial molal volume of the initial-state substrate, benzyl chloride, in each of the solvents and in the aqueous ethyl alcohol solvents of ref 1 is measured and shown to account for the major part of the extremum behavior. The solvent dependence of the partial molal volume of the transition state is shown to be remarkably similar to that of various inorganic salts in the same solvents.

In a previous publication[1] we reported a study of the effect of pressure on the solvolysis of benzyl chloride in aqueous ethyl alcohol. It was found that, as the alcoholic content of the solvent increases, the activation volume at atmospheric pressure, $\Delta V_0^{\ddagger}$, exhibits extremum behavior similar to that previously reported for the activation enthalpy, $\Delta H^{\ddagger}$, and entropy, $\Delta S^{\ddagger}$.[2] At that time no data were available to indicate whether variations in the volume of the initial or the transition state, or both, are responsible for the extremum behavior.

---

(1) J. B. Hyne, H. S. Golinkin, and W. G. Laidlaw, *J. Am. Chem. Soc.*, **88**, 2104 (1966).

(2) J. B. Hyne, R. Wills, and R. E. Wonkka, *ibid.*, **84**, 2914 (1962).