monohydrate: CD (H_2O) $\Delta\epsilon$ −0.6 (278 nm), −0.65 (240 nm); $[\alpha]^{20}{}_D$ +12.3° (H_2O, 0.005).

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Registry No. 7, 55314-19-7; (−)-C_{12}CPB, 91238-47-0; (+)-C_{12}CPB, 91238-48-1; dodecyl bromide, 143-15-7.

Di-*tert*-butyl Peroxide: Can Its Photolysis Be Quenched by Carbon Tetrachloride and Why Is It Stable at Room Temperature?[1]

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It has been reported[3] that photolysis of acetonitrile solutions containing di-*tert*-butyl peroxide and carbon tetrachloride in the cavity of an EPR spectrometer yielded the spectra of methyl and trichloromethyl radicals, even when the carbon tetrachloride was screened from direct photolysis.

The methyl radical was presumed[3] to have been formed by β-scission of *tert*-butoxyl, which was accelerated by the polar solvent, eq 1 and 2.[4] However, literature data[5]

$$t\text{-BuOOBu-}t \xrightarrow{h\nu} 2t\text{-BuO}\cdot \qquad (1)$$

$$t\text{-BuO}\cdot \rightarrow (\mathrm{CH_3})_2\mathrm{CO} + \dot{\mathrm{C}}\mathrm{H}_3 \qquad (2)$$

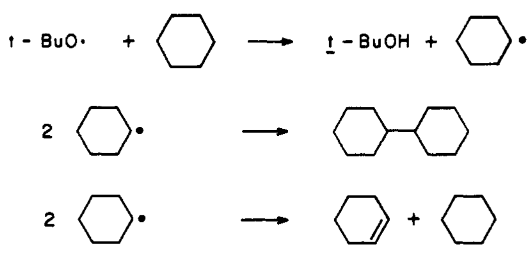
indicated that the rate of chlorine abstraction by methyl from carbon tetrachloride was too slow to have given rise to trichloromethyl under the reaction conditions. It was therefore concluded[3] that carbon tetrachloride was acting as a quencher of the peroxide photolysis to yield $\cdot$Cl and $\cdot CCl_3$.

These experimental results have been confirmed in our laboratory. However, their original interpretation[3] conflicts with gas-phase[6,7] and theoretical[8] work which suggest that the singlet excited states of dialkyl peroxides are dissociative and therefore ought not to be quenched by carbon tetrachloride. We now describe a number of experiments designed to resolve this problem.

The decomposition of carbon tetrachloride can be sensitized by ketones[9] whose triplet energy is greater than the carbon–chlorine bond dissociation energy of 73 kcal mol^{-1}.[10] Thus, photolysis of benzophenone (0.1 M) in carbon tetrachloride at 25 °C did not give rise to an EPR spectrum of trichloromethyl since the triplet energy of the ketone[11] is only 68.6 kcal mol^{-1}. However, trichloromethyl was observed when di-*tert*-butyl peroxide was added to the reaction mixture under conditions where the benzophenone absorbed essentially all of the light. Clearly the ketone could not have transferred enough energy to the peroxide for the latter to have *sensitized* the decomposition of the carbon tetrachloride. However, the ketone certainly provided sufficient energy to induce the decomposition of the peroxide.[12] Hence, trichloromethyl must have been formed in a chemical reaction between one of the products of the peroxide decomposition and carbon tetrachloride.

In a second set of experiments, the mixtures described in Table I were photolyzed in a merry-go-round apparatus at 35 °C. The compositions of the mixtures and the choice of photolysis wavelengths ensured that the light was being absorbed by the peroxide alone and that the same amount of light was absorbed by each sample. The samples were photolyzed to low conversions <1.0% so to avoid complications from secondary reactions. Products were identified by mass spectrometry and were quantified by GC using a 20 ft, 12% OV-101 column. *tert*-Butylbenzene was used as an internal standard, and pure samples of each of the products were used as sensitivity calibrants.

Sample I contained di-*tert*-butyl peroxide and cyclohexane and acted basically as an actinometer. Photolysis gave *tert*-butyl alcohol as the only peroxide-derived product. Bicyclohexyl was also detected but cyclohexene could not be resolved from cyclohexane at these low levels of conversion, thus making it impossible to quantify the radical combination–disproportionation yields, eq 3–5. The yield of *tert*-butyl alcohol divided by the photolysis time gave the rate of initiation, R_i, as 1.04×10^{-5} M s^{-1} under our experimental conditions.



(3)

(4)

(5)

Sample II was similar to I except that it contained carbon tetrachloride. Nevertheless, the yiels of *tert*-butyl alcohol were the same, within experimental error, in both cases. This confirms that the photolysis of the peroxide was neither quenched physically nor chemically by carbon tetrachloride.

The yield of cyclohexyl chloride was greater than expected on the basis of reactions 6 and 7 alone and chloroform was also detected as a product. These results imply that there was significant hydrogen abstraction from cyclohexane by the trichloromethyl radical, eq 8. The product yields are exactly consistent with the stoichiometry dictated by this additional process. Thus eq 6 and 8 represent the propagation steps of a chain reaction. Moreover, since no bicyclohexyl was detected, reaction 7 must have been the termination step, i.e., $k_6 \gg k_8$. Ap-

(6)

$$2\ \cdot\mathrm{CCl_3} \longrightarrow \mathrm{C_2Cl_6} \qquad (7)$$

(8)

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[3] Paul, H.; Small, R. D., Jr.; Scaiano, J. C. *J. Am. Chem. Soc.* **1978**, *100*, 4520.

[4] Walling, C.; Wagner, P. J. *J. Am. Chem. Soc.* **1964**, *86*, 3368.

[5] Trotman-Dickenson, A. F.; Milne, G. S. *Natl. Stand. Ref. Data Ser., Natl. Bur. Stand.* **1968**, *9*, 51.

[6] Calvert, J. G.; Pitts, J. N. J. "Photochemistry"; Wiley: New York, 1966; pp 172, 443.

[7] Dorer, F. H.; Johnson, S. N. *J. Phys. Chem.* **1971**, *75*, 3651.

[8] Evleth, E. M. *J. Am. Chem. Soc.* **1976**, *98*, 1637.

[9] Scaiano, J. C., unpublished results.

[10] McMillen, D. F.; Golden, D. M. *Annu. Rev. Phys. Chem.* **1982**, *33*, 493.

[11] Murov, S. L. "Handbook of Photochemistry"; Marcel Dekker: New York, 1973; p 3.

[12] Scaiano, J. C.; Wubbels, G. G. *J. Am. Chem. Soc.* **1981**, *103*, 640.

Table I. Product Yields after Photolysis of Samples I–III[a]

	reactants, M			products, mM					
	[t-BuOOBu-t]	[c-C_6H_{12}]	[CCl_4]	[t-BuOH]	[$(CH_3)_2\overline{CCH_2O}$]	[c-$C_6H_{11}Cl$]	[C_2Cl_6]	[$HCCl_3$]	[CH_3Cl]
I	2.71	4.62		25 ± 1					
II	2.71	2.78	2.07	27 ± 2		45 ± 2	14 ± 1	15 ± 1	
III	2.71		5.18	67 ± 3	72 ± 3		8 ± 1		10 ± 2[b]

[a] Based on the results of duplicate or triplicate experiments. [b] Acetone was a complementary product, but its low yield and poor GC response (flame ionization) precluded accurate analysis.

plication of the normal kinetic expression[13] for a chain reaction combined with the value obtained for R_i (vide supra) and the data in Table I gave $k_8 = 50$ M^{-1} s^{-1} at 35 °C in excellent agreement with gas-phase values of 16 M^{-1} s^{-1} [16] and 60 M^{-1} s^{-1}.[17]

Sample III contained no cyclohexane but gave approximately 3 times more *tert*-butyl alcohol than the other samples, together with an essentially equal yield of isobutylene oxide.[18] This observation is consistent with a chain reaction involving reactions 9 and 10 as the propagation steps.

$$t\text{-BuO}\cdot + t\text{-BuOOBu-}t \rightarrow t\text{-BuOH} + \dot{C}H_2C(CH_3)_2OOBu\text{-}t \quad (9)$$

$$\dot{C}H_2C(CH_3)_2OOBu\text{-}t \rightarrow t\text{-BuO}\cdot + (CH_3)_2\overline{COCH_2} \quad (10)$$

The formation of hexachloroethane and chloromethane implies that the squence of reactions 2, 11,

$$\cdot CH_3 + CCl_4 \rightarrow CH_3Cl + \dot{C}Cl_3 \quad (11)$$

and 7 was partly responsible for chain termination. In addition, the fact that the yield of hexachloroethane was smaller in III than II suggests that some termination was taking place via other processes.

The above results show that the photolysis of di-*tert*-butyl peroxide is not quenched by carbon tetrachloride and that the observation by EPR of trichloromethyl radicals[3] was almost certainly due to reactions 1, 2, and 11.

Two corollaries follows: First, k_{11} must be $>10^2$ M^{-1} s^{-1} at 25 °C and not 9 M^{-1} s^{-1} [5] for EPR observation of $\cdot CCl_3$ to have been possible.[19,20] Second, the results imply that the normal rate of thermolysis of the peroxide at 25 °C[21] would be sufficient to initiate its decomposition via reactions 9 and 10. This would proceed with a chain length of ca. 10^6 and a rate of ca. 10^{-5} M^{-1} s^{-1} which would lead to substantial degradation of the peroxide within a few weeks.[22] The reason that this does not normally occur is presumably that dissolved oxygen, hydroperoxide impurities, and especially isobutylene oxide itself, which are all highly reactive toward *tert*-butoxyl radicals,[26] function as chain-breaking inhibitors.

Experimental Section

With the exception of di-*tert*-butyl peroxide, all of the materials used in this work were commercially available in high purity and were used as received. Di-*tert*-butyl peroxide was treated with aqueous silver nitrate solution so as to remove olefinic impurities. It was then washed with water and was dried over magnesium sulfate. It was finally passed through a column of alumina to remove hydroperoxide impurities.

Photolyses were carried out in a merry-go-round reactor, under conditions where the peroxide was the only light absorbing reactant. Thus, the reactor was fitted with 350-nm lamps and their relatively broad spectral output was reduced by the use of filters which had only 15% transmission at 330 nm.

Products were identified by GC/MS (Hewlett-Packard 5995). They were quantified by GC analysis (20 ft, 12% OV-101 column; Varian 3700 instrument); see text for further details.

Acknowledgment. We thank Drs. J. C. Scaiano (NRCC) and P. Engel (Rice University) for helpful discussions and suggestions.

Registry No. Di-*tert*-butyl peroxide, 110-05-4; carbon tetrachloride, 56-23-5; cyclohexane, 110-82-7; trichloromethyl, 3170-80-7.

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(13) d[$HCCl_3$]/dt = k_8[c-C_6H_{12}]$(R_i/2k_7)^{1/2}$. A value of $2k_7 = 5 \times 10^9$ M^{-1} s^{-1} was taken for this calculation on the basis of literature data for $2k_7$ at −40 °C[14] combined with data for the temperature dependence of diffusion-controlled reactions.[15]

(14) Paul, H. *Int. J. Chem. Kinet.* **1979**, *11*, 495.

(15) Schuh, H.-H.; Fischer, H. *Helv. Chim. Acta* **1978**, *61*, 2130.

(16) White, M. L.; Kuntz, R. R. *Int. J. Chem. Kinet.* **1971**, *3*, 127.

(17) Currie, J. L.; Sidebottom, H. W.; Tedder, J. M. *Int. J. Chem. Kinet.* **1974**, *6*, 481.

(18) Bell, E. R.; Rust, F. F.; Vaughan, W. E. *J. Am. Chem. Soc.* **1950**, *72*, 337. Bloodworth, A. J.; Davies, A. G.; Griffin, I. M.; Muggleton, B.; Roberts, B. P. *Ibid.* **1974**, *96*, 7599.

(19) Griller, D.; Ingold, K. U. *Acc. Chem. Res.* **1980**, *13*, 193.

(20) Recent gas-phase data support this conclusion and give $k_{11} = 75$ M^{-1} s^{-1} at 25 °C, see: Matheson, I. A.; Tedder, J. M.; Sidebottom, H. W. *Int. J. Chem. Kinet.* **1982**, *14*, 1033.

(21) Koenig, T. In "Free Radicals"; Kochi, J. K., Ed.; Wiley: New York, 1973; Vol. I, p 122.

(22) Obtained by application of the normal expression for chain reactions, cf.: ref 13. Reaction 9 must be rate determining since $k_9 \simeq 5 \times 10^4$ M^{-1} s^{-1} [23] while $k_{10} = 1.1 \times 10^6$ s^{-1}.[18,24] The termination step should therefore be 2t-BuO· → products, for which the rate constant is 1.3×10^9 M^{-1} s^{-1}.[25]

(23) Estimated from the rate constant for hydrogen abstraction from the methyl groups of pentane; Griller, D.; Ingold, K. U.; Jackson, R. A.; Nazran, A. S., unpublished results.

(24) Chatgilialoglu, C.; Ingold, K. U.; Scaiano, J. C. *J. Am. Chem. Soc.* 1981, *103*, 7739.

(25) Wong, S. K. *Int. J. Chem. Kinet.* **1981**, *13*, 433.

(26) By analogy with ethylene oxide,[27] the rate constant for hydrogen abstraction from isobutylene oxide must be ca. 1×10^6 M^{-1} s^{-1}.

(27) Maltesta, V.; Scaiano, J. C. *J. Org. Chem.* **1982**, *47*, 1455.

Metal-Mediated Concomitant Silyl Ether Cleavage/Cyclization Reactions To Construct Bicyclic Piperazinediones and a New Polymer-Supported Mercury(II) Perchlorate

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Recently, we developed[1] a short and efficient cyclization reaction to construct the bicyclic piperazinedione ring system present in the novel antibiotic bicyclomycin.[2] The bicyclic piperazinediones 2 have proven to be versatile intermediates for elaboration into structurally diverse bicyclomycin analogues[3] as well as potential intermediates for the total synthesis of the natural product.[4] During the

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(1) Williams, R. M.; Anderson, O. P.; Armstrong, R. W.; Josey, J.; Meyers, H.; Eriksson, C. *J. Am. Chem. Soc.* **1982**, *104*, 6092.

(2) See the citations in ref 1 and 3 for biological activity, structure elucidation, isolation, and synthetic approaches to bicyclomycin (bicozamycin, aizumycin, The Merck Index, 10th ed., 1983, p 1213).

(3) Williams, R. M.; Dung, J-S.; Josey, J.; Armstrong, R. W.; Meyers, H. *J. Am. Chem. Soc.* **1983**, *105*, 3214.

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