Table II. Methyl Carbon Kinetic Isotope Effects[a]

Solvent	Temp, °C	f_{max}[b]	n[c]	k_{12}/k_{13}
Cumene	44.7	0.02	4	1.0038 ±0.0005
Isooctane	44.4	0.13	3	1.0029 ±0.0007
	80			"*1.005–1.010*"[d]

[a] Uncertainties are standard deviations; italicized entries are from other laboratories. [b] Maximum extent of partial decomposition. [c] Number of independent partially decomposed samples analyzed. [d] Reference 5.

that at the carboxyl carbon by almost an order of magnitude[13] (Table II).

Finally, we would hope that the reproducibility noted in Table I might carry with it the implication that similarly obtained results from our own and other laboratories be (at least initially) regarded as no less reliable.

Acknowledgment. Financial support was provided by the National Science Foundation under Grants GP-3527 and GP-7479 and by the A.F.O.S.R. under Grant 142-163.

(13) As empirical orientation, the acetylenic and nitrile k_{12}/k_{13} measured for dicyanoacetylene addition to cyclopentadiene at 0° are 1.0204 and 1.0003 (C. B. Warren, Ph.D. Thesis, Cornell University, Ithaca, N. Y., 1970).

M. J. Goldstein, H. A. Judson, M. Yoshida
Department of Chemistry, Cornell University
Ithaca, New York 14850

Received February 11, 1970

Reaction of Excited Triphenylcarbonium Ion with Oxygen[1a]

Sir:

In the relatively unexplored area of carbocation photolysis,[1b] the triphenylcarbonium ion case possesses special significance because of the widespread interest in the photochemistry of structurally related dyes, especially those used as sensitizers for singlet oxygen reactions. We describe herein the irradiation-induced behavior of the parent trityl case with oxygen.

When triphenylcarbonium ion in 3.3% H_2SO_4–96.5% CH_3CO_2H–0.2% H_2O was photolyzed under oxygen with visible light,[2] there were formed benzophenone (37%), diphenylmethylenedioxybenzene (I; 30%),[5] and a substance, $C_{21}H_{18}O_4$,[6] mp 116–118° (11%), assigned structure II. In addition to the molecular ion at 334, the mass spectrum of II displayed a first fragmentation peak at 302 ($-O_2$), then *inter alia* 274 ($-CH_3COOH$) and 243 (base peak, $-O_2$ and CH_3CO_2).[6] The uv spectrum revealed maximal absorption at 260 nm (ϵ 3600), while carbonyl absorption in the ir fell at 5.72 μ. Proton resonances ($CDCl_3$ solvent, 60 MHz) appeared at τ 7.92 (3 H, singlet, acetate), 4.85–3.90 (5 H, complex multiplet), and 2.67 (10 H, aromatic singlet). Catalytic reduction (5% Rh–C in aqueous methanol) led to a triol monoacetate (III) which was inert to sodium metaperiodate. In the infrared, the reduction product displayed peak absorption at 2.92 ($-OH$) and 5.81 (acetate) μ. An nmr spectrum ($CDCl_3$, HA 100) included the following signals: τ 8.00 (3 H, singlet, acetate), 8.6–7.8 (4 H, multiplet, methylene), 6.65 (1 H, broad singlet, hydroxyl), 5.78 (1 H, multiplet, $>CHO$), 5.47 (1 H, broad singlet, hydroxyl), 5.06 (1 H, multiplet, olefinic), 4.68 (1 H, multiplet, olefinic), and 2.76 (10 H, singlet aromatic). After D_2O exchange, the τ 5.47 and 6.65 signals disappeared while the τ 5.78 peak sharpened into a doublet.

At lower acid concentrations (1% H_2SO_4) triphenylcarbonium ion provided on photolysis an aldehyde acetate (IV) in addition to the above products. This substance possessed (high-resolution mass spectrum) the formula $C_{21}H_{18}O_4$.[6] In addition to the molecular ion, the low-resolution mass spectrum included fragmentation peaks at m/e 292 ($-CH_2CO$), 274 (base peak, $-CH_3CO_2H$), and 245 ($-CH_3CO_2H$ and CHO). Carbonyl absorption appeared in the ir at 5.71 and 5.88 μ and in the uv at 298 and 309 nm (conjugated). In an nmr analysis, the aldehyde displayed signals at τ 8.25 (3 H, singlet), 4.20–3.70 (4 H, complex multiplet), 2.81 (10 H, singlet), and 0.75 (1 H, singlet). Saponification provided the expected aldehyde alcohol, whereas reduction with sodium borohydride effected simple conversion of the aldehyde function to the corresponding alcohol (λ_{max} 264, 270 nm).

Because under conditions of complete light absorption the rate of disappearance of triphenylcarbonium ion was independent of its concentration, a mechanism involving the formation of singlet oxygen and its subsequent reaction with ground-state carbonium ion (or trityl acetate) seems unlikely.[7] Furthermore, the ready reaction of singlet oxygen with triphenylcarbonium ion would not be expected, as singlet oxygen is thought to be electrophilic.[7] A simple mechanism consistent with the above observations is shown in Scheme I.

It seems most reasonable to assume that it is the excited triplet state of the carbonium ion that is under-

---

(1) (a) Part II of a series concerned with the photolysis of triphenylcarbonium ion; (b) the first studies involving identification of photoproducts derived from carbonium ion cases were reported by E. E. van Tamelen, T. M. Cole, R. Greeley, and H. Schumacher, *J. Amer. Chem. Soc.*, **90**, 1372 (1968).

(2) All photolyses were carried out using a 450-W Hanovia medium-pressure lamp surrounded by a uranium(VI) glass filter. The carbonium ion source was triphenylcarbinol (*ca.* 10^{-3} *M*). Control experiments indicated that covalent trityl compounds are not photolyzed under these conditions. Furthermore, energy transfer from triplet triphenylcarbonium ion to covalent trityl compounds would be highly endothermic. On the basis of its phosphorescence spectra trityl cation has $E_T \sim 50$ kcal/mol.[3] On the basis of published phosphorescence data, covalent trityl species have $E_T \sim 70$ kcal/mol.[4]

(3) In 96% sulfuric acid at room temperature triphenylcarbonium ion exhibits weak fluorescence ($\phi_F \sim 0.01$–0.001) with maxima at *ca.* 520 and 540 nm. At −196° in a sulfuric acid glass trityl cation has a phosphorescence maximum at 545 nm ($\phi_P/\phi_F \sim 20$) (we thank Professor L. Stryer for the fluorescence and phosphorescence measurements). From its ϵ of 4×10^4 at λ_{max} 410, 430 nm and the absence of fluorescence under nitrogen ($\phi_F < 0.001$) in the 3.3% sulfuric acid-acetic acid system, the singlet lifetime of the trityl cation can be roughly estimated to be $<2.5 \times 10^{-12}$ sec in this system (J. G. Calvert and J. N. Pitts, Jr., "Photochemistry," Wiley, New York, N. Y., 1966, p 174; N. J. Turro, "Molecular Photochemistry," W. A. Benjamin, New York, N. Y., 1967, p 54), which would seem to be too short to allow appreciable reaction with oxygen at *ca.* 10^{-2} *M* (E. W. Washburn, Ed., "International Critical Tables of Numerical Data, Physics, Chemistry and Technology," Vol. III, McGraw-Hill, New York, N. Y., 1928, p 263).

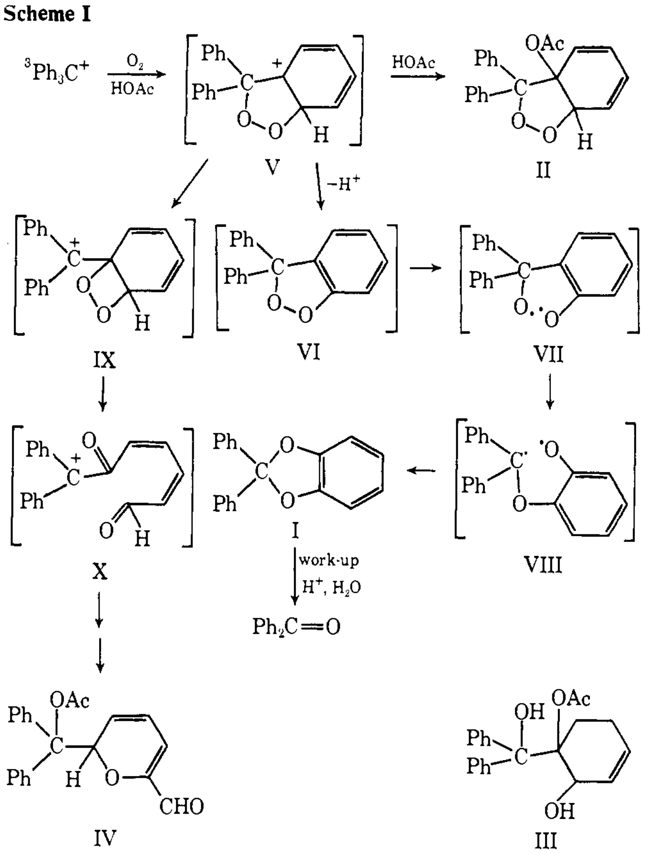
(4) Yu. I. Kozlov and D. N. Shigorin, *Dokl. Akad. Nauk SSSR*, **161**, 871 (1965); *Chem. Abstr.*, **63**, 6528 (1965).

(5) The 1,2-diphenylmethylenedioxybenzene was identified by spectral and mixture melting point comparison with authentic material.

(6) The high-resolution mass spectrum was obtained on a MS-9 direct inlet machine. The low-resolution mass spectrum was obtained on an Atlas direct inlet machine.

(7) C. S. Foote, *Accounts Chem. Res.*, **1**, 104 (1968).

Scheme I



going this reaction, especially since in this system no fluorescence could be observed.[3] The homolysis of VI to VII would be expected on the basis of findings that diaryl peroxides are stable only at very low temperatures, decomposing upon warming to aryloxy radicals.[8,9] The conversion of VII to VIII is analogous to the known conversion of triphenylmethoxy radical to the more stable diphenylphenoxymethyl radical,[10] while the four-membered peroxide IX would be expected by precedent[11–14] to cleave to the keto aldehyde.

It has not yet been determined whether singlet oxygen is produced in this system. However, preliminary results indicate that the excited triplet carbonium ion is quenched by oxygen to an extent greater than can be accounted for by the formation of the peroxide-derived products.[15]

Acknowledgment. The authors are grateful to the Army Research Office—Durham (Project No. CRD-AA-5227-C) and the Petroleum Research Fund (Grant 2892 (A1,4)), administered by the American Chemical Society, for support. Also, thanks are due Dr. Lois Durham for consultation on nmr spectra and to Professor L. Altman for helpful discussions.

---

(8) C. Walling, "Free Radicals in Solution," Wiley, New York, N. Y., 1957, p 466.

(9) A heterolytic mechanism, perhaps involving initial protonation of a peroxide oxygen, could also be invoked to rationalize the formation of I from VI.

(10) H. Wieland, *Ber.*, **44**, 2533 (1911).

(11) Pitts, *et al.*, isolated succindialdehyde from the photooxidation of benzene and postulated a related four-member peroxide: K. Wei, J. Mani, and J. Pitts, Jr., *J. Amer. Chem. Soc.*, **89**, 4225 (1967).

(12) E. H. White, J. Wiecko, and D. F. Roswell, *ibid.*, **91**, 5194 (1969).

(13) W. Fenical, D. R. Kearns, and P. Radlick, *ibid.*, **91**, 3398 (1969).

(14) K. R. Kopecky and C. Mumford, *Can. J. Chem.*, **47**, 709 (1969).

(15) For example, in 72% aqueous sulfuric acid oxygen slowed the photodimerization[1b] by a factor of 4 but did not form any adducts with triphenylcarbonium ion.

(16) National Institutes of Health Predoctoral Fellow, 1965–1968; address correspondence to Department of Chemistry, Columbia University, New York, N. Y. 10027.

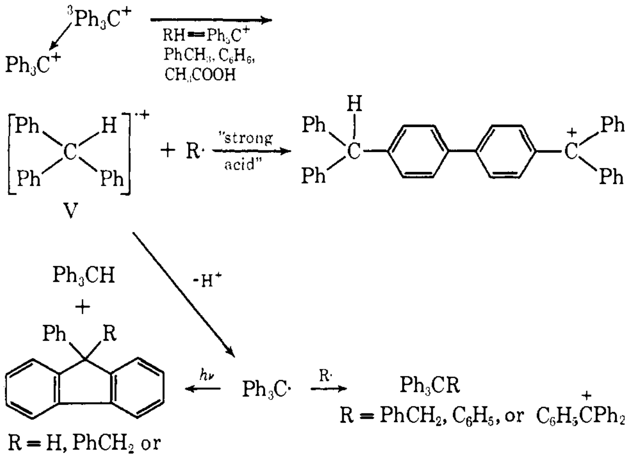
E. E. van Tamelen, T. M. Cole, Jr.[16]
Department of Chemistry, Stanford University
Stanford, California 94305

Received October 15, 1969

Photolysis of Triphenylcarbonium Ion under Nitrogen[1]

Sir:

In Table I are listed the results of the photolysis of triphenylcarbonium ion in various systems under nitrogen.[2] These products are consistent with the mechanistic scheme shown below in which the primary photochemical process is the abstraction of a hydrogen atom by the excited triplet of triphenylcarbonium ion to form V. The acidity of the medium, the identity of the hydrogen donor RH, and the intensity of light capable of photolyzing trityl radical determine the ultimate product composition.



The following results support the involvement of the excited triplet state of triphenylcarbonium ion: in expt 4 the dimerization could be quenched (by $FeSO_4$, NaBr, and NaCl) without diminishing the trityl cation fluorescence; in expt 1–3 no fluorescence was observed, and when expt 1 was carried out under oxygen, none of the anaerobic products were obtained.[3]

The formation of cation-radical V from triplet trityl cation receives support from the formation of I–III in expt 4 and II in expt 6. When expt 4 was carried out using *ortho*- and *para*-deuterated triphenylcarbonium ion, the dimerization was slowed by a factor of 2.5, consistent with a rate-determining hydrogen atom abstraction from the *para* position of a ground-state

---

(1) Part III of a series concerned with the photolysis of triphenylcarbonium ion.

(2) E. E. van Tamelen, T. M. Cole, R. Greeley, and H. Schumacher, *J. Amer. Chem. Soc.*, **90**, 1372 (1968).

(3) E. E. van Tamelen and T. M. Cole, Jr., *ibid.*, **92**, 4123 (1970).