

Singlet Oxygen in the Environmental Sciences. IV.¹

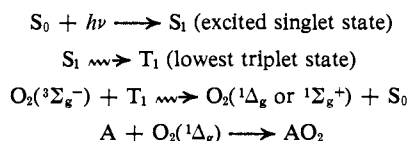
Kinetics of the Reactions of Oxygen (¹Δ_g) with Tetramethylethylene and 2,5-Dimethylfuran in the Gas Phase^{2a}

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Abstract: Electronically excited molecular oxygen, O₂(¹Δ_g) generated in a microwave discharge was treated in the gas phase with tetramethylethylene (TME) and 2,5-dimethylfuran (DMF). Infrared spectra and glpc analysis of the gas stream showed that under suitable conditions the reactions of O₂(¹Δ_g) with TME and DMF give essentially 100% yields of 2,3-dimethyl-3-hydroperoxy-1-butene (**2**) and the ozonide 2,3,7-trioxa-1,4-dimethylbicyclo[2.2.1]-5-heptene (**4**), respectively. Absolute values for the bimolecular rate constants at 22° were $k_{\text{TME}} = (1.0 \pm 0.5) \times 10^5$ and $k_{\text{DMF}} = (3.7 \pm 1.4) \times 10^6$ l. mole⁻¹ sec⁻¹. The quenching of O₂(¹Δ_g) by TME was predominately chemical, forming the hydroperoxide. However, both physical and chemical quenching were observed in the ¹O₂-DMF system at about the same rate. Mechanistic implications of these results are discussed.

The oxidation of many organic compounds, in solution, using oxygen and suitable photosensitizers is now known to involve molecular oxygen in the electronically excited ¹Δ_g state.^{3,4} The simplified reaction scheme for such Kautsky type photooxidations is



where S is the photosensitizer and A the compound being oxidized. Much of the evidence for the involvement of O₂(¹Δ_g) in such oxidations⁴ has come from investigations of oxidations in solution, brought about by the action of H₂O₂ mixed with NaOCl, which is known to produce this electronically excited molecule.^{5,6}

It has recently been confirmed experimentally^{1,7} that O₂(¹Δ_g) is produced by energy transfer in the gas phase, the donor molecules being photoexcited triplet states of benzene and naphthalene derivatives. These results and recent evidence for other modes of formation of O₂(¹Δ_g) in gas phase systems^{8,9} support the

(1) Part III: R. P. Steer, J. L. Sprung, and J. N. Pitts, Jr., *Environ. Sci. Technol.*, **3**, 946 (1969).

(2) (a) Presented in part at the Symposium on Toxicologic and Epidemiologic Bases for Air Quality Criteria, 62nd Annual Meeting, Air Pollution Control Association, New York, N. Y., June 1969, and also at the Symposium on Chemical Reactions in Urban Atmospheres, General Motors Research Laboratory, Detroit, Mich., Oct 6, 1969; (b) Mount (Allison) University, Sackville, New Brunswick, Canada; (c) University College, Cardiff, Great Britain; (d) author to whom correspondence should be addressed.

(3) K. Gollnick, *Advan. Photochem.*, **6**, 1 (1968).

(4) C. S. Foote, *Science*, **162**, 963 (1969); *Accounts Chem. Res.*, **1**, 104 (1968).

(5) J. S. Arnold, R. J. Browne, and E. A. Ogryzlo, *Photochem. Photobiol.*, **4**, 963 (1965).

(6) A. U. Khan and M. Kasha, *J. Amer. Chem. Soc.*, **88**, 1574 (1966).

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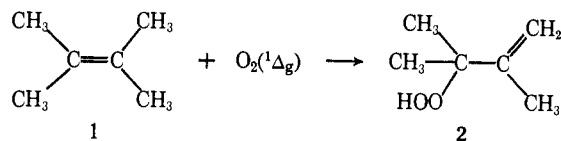
(8) A. U. Khan, J. N. Pitts, Jr., and E. B. Smith, *Environ. Sci. Technol.*, **1**, 656 (1967); J. N. Pitts, Jr., A. U. Khan, E. B. Smith, and R. P. Wayne, *ibid.*, **3**, 241 (1969).

(9) Recent reviews: R. P. Wayne, *Advan. Photochem.*, **7**, 311 (1969); J. N. Pitts, Jr., *Advan. Environ. Sci.*, **1**, 289 (1969); J. N. Pitts, Jr., *J. Air Poll. Control Assoc.*, **19**, 658 (1969).

proposals that it may be an important environmental oxidant, for example, in photochemical air pollution.

Data on reactions of O₂(¹Δ_g) with organic compounds in the gas phase are limited and conflicting.⁹ One of the most reactive compounds toward O₂(¹Δ_g) in solution is tetramethylethylene (TME, **1**),⁴ yet Corey and Taylor¹⁰ were unable to detect any reaction between this olefin and O₂(¹Δ_g), generated by an electrodeless discharge through O₂(³Σ_g⁻). The deactivation of O₂(¹Δ_g) by ethylene has been observed,¹¹ but again no chemical reaction was reported. Recently, gas-phase reactions of O₂(¹Δ_g) with 1,3-cyclohexadiene and α-terpinene have been reported by Murray and Kaplan¹² but no reaction with TME was detected.

In direct contrast, Winer and Bayes¹³ found that O₂(¹Δ_g), produced by the discharge method, consumed about 10% of the TME, added to the oxygen stream. The glpc retention time and mass spectrum of the product indicated that this was 2,3-dimethyl-3-hydroperoxy-1-butene (**2**). The hydroperoxide, **2**, is the



sole product of the sensitized photooxidation of TME in solution.

We have recently reported¹⁴ that TME will in fact react with O₂(¹Δ_g) in the gas phase to produce **2**, in essentially 100% yield. In addition, we also established that the ozonide, **4**, is formed in 100% yield in the gas-phase reaction of O₂(¹Δ_g) and 2,5-dimethylfuran (DMF, **3**).

(10) E. J. Corey and W. C. Taylor, *J. Amer. Chem. Soc.*, **86**, 3881 (1964).

(11) A. M. Falick, B. H. Mahan, and R. J. Meyers, *J. Chem. Phys.*, **42**, 1837 (1965).

(12) R. W. Murray and M. L. Kaplan, *J. Amer. Chem. Soc.*, **90**, 4161 (1968); **91**, 5358 (1969).

(13) A. M. Winer and K. D. Bayes, *J. Phys. Chem.*, **70**, 302 (1966).

(14) A. D. Broadbent, W. S. Gleason, J. N. Pitts, Jr., and E. Whittle, *Chem. Commun.*, 1315 (1968).

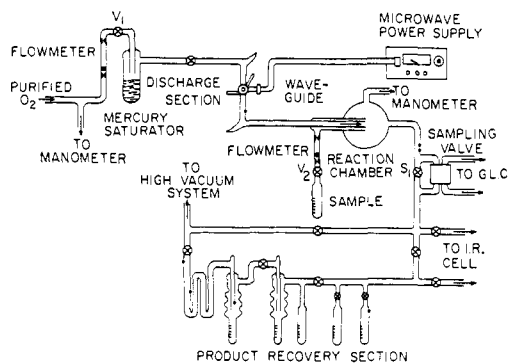
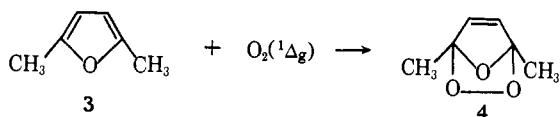


Figure 1. Apparatus for the generation and reaction of singlet oxygen.

In this paper, qualitative and quantitative product and kinetic studies of the above gas phase reactions are described, and discussed in relation to reactions of $O_2(^1\Delta_g)$ with TME and DMF in solution, as well as to certain environmental problems.



Experimental Section

Materials. TME (J. T. Baker Chemical Co.) and DMF (Research Organic/Inorganic Chemical Co.) were purified by treatment with alumina followed by fractional distillation at atmospheric pressure. Analysis by glpc showed that each contained less than 0.1% impurities. Both compounds, but particularly DMF, are unstable in the presence of air and light. The development of impurities was slowed considerably by storing the liquids under N_2 in a refrigerator.

Apparatus. The main part of the apparatus is shown in Figure 1. Ultrapure oxygen (Matheson Co.) entered through a flowmeter and a precision needle valve, V_1 . The gas was then mixed with mercury vapor and passed along a 13 mm o.d. quartz tube, where it was subjected to a microwave discharge, produced by a tuneable waveguide,¹⁵ connected to a 2450-MHz Raytheon microwave generator, through a Bendix power meter. Such a discharge produces atomic oxygen and electronically excited molecular oxygen in the $^1\Delta_g$ and $^1\Sigma_g^+$ states. Mercuric oxide was deposited immediately downstream from the discharge. This and the mercury vapor acted as efficient scavengers of atomic oxygen and ozone. The initially observed NO_2 airglow, resulting from traces of N_2 in the oxygen, rapidly faded and was not observed beyond the HgO deposit. The inherent radiative lifetime of $O_2(^1\Sigma_g^+)$ is 7 sec and, because collisional deactivation of this excited state is considered efficient,^{5,6} we assumed that the gas entering the spherical reaction vessel, through the inner of two concentric nozzles, consisted only of $O_2(^1\Delta_g)$ and ground state $O_2(^3\Sigma_g^-)$. The discharge was surrounded by a can of magnetic shielding metal, whose diameter was about equal to the wavelength of the microwave radiation. This reflects radiation not absorbed and maximizes the $O_2(^1\Delta_g)$ concentration.

The organic substrate was degassed and its vapor admitted to the reaction chamber through the outer nozzle, after passing through a precision needle valve, V_2 , and a calibrated capillary flowmeter. Mixing of the organic substrate and $O_2(^1\Delta_g)$ occurred at the nozzles in the center of the reaction vessel, which had a volume of 2100 cm^3 . A spherical chamber was used to minimize wall quenching of $O_2(^1\Delta_g)$. The O_2 flow rate was usually about 80 cm^3/sec , at a reaction-chamber pressure of about 7 Torr. The gases leaving the chamber passed through a Teflon stopcock, S_1 , which controlled the flow rate. In parallel with S_1 was a Carle microsampling valve, which was used to inject a sample of the gas stream into a gas chromatograph. The samples were analyzed on a 3 ft \times $1/8$ in. or 9 in. \times $1/8$ in. column of Nujol on firebrick at 60°, using flame ionization

detection. The gas stream could also be diverted through a 10-m path length infrared cell mounted in a Perkin-Elmer 221 spectrophotometer. This was used to record the vapor phase ir spectra of reactants and products. The gas stream finally passed through three traps which effected complete recovery of material, even at high linear flow rates.

The spherical reaction vessel was only used for reactions in which high conversions to products were desired for identification purposes. Experiments with the NO_2 air-glow showed that mixing of gases in the spherical reaction vessel was not homogeneous, so that contact times could not be accurately determined. This reactor was therefore replaced by a 100-cm linear reactor (i.d. 31 mm), which had several inlet ports for introducing the vapors of TME or DMF. Reproducible O_2 flow rates, at selected pressures, were established by inserting a Teflon disk, with a single hole of suitable diameter, at the end of the flow tube. Observation of the NO_2 airglow, from a small sample of NO introduced into the stream of O_2 in a Hg free system showed that the flow rate was constant along the length of the linear reactor and equal to that measuring using a calibrated flowmeter. A double spiral of CoO wire was used to deactivate any unreacted $O_2(^1\Delta_g)$. The efficiency of the CoO wire spiral in deactivating $O_2(^1\Delta_g)$ was tested by initially placing it in the linear reactor so that TME could be injected either above or below it. The amount of TME consumed, when injected below the spiral, was less than 1% of that consumed when injected above it. This would indicate that the CoO spiral was at least 99% effective in deactivating unreacted $O_2(^1\Delta_g)$. The CoO wire was finally inserted into the system 5 cm above the glpc sampling port. Without the wire the contact time, t , could not be measured, because the rate of flow through the sampling loop was unknown. Contact times, calculated simply on the basis of linear flow along the main reaction tube, were therefore too low by an unknown factor and gave higher values of the rate constants (see Figure 6). Using the CoO wire, the point of complete reaction quenching was precisely defined, and the contact time was simply calculated by dividing the linear flow rate by the distance between the mixing inlet and the CoO wire. The CoO wire did not effect the determination of the singlet oxygen concentration since if sufficient TME was injected to remove all the singlet oxygen within the reaction time then none remained to be deactivated by the wire. This system was used to investigate the kinetics of $O_2(^1\Delta_g)$ with TME and DMF.

All experiments were performed at room temperature (22°).

Results and Discussion

Product Studies. Tetramethylethylene. In early experiments using the spherical reactor, TME vapor was injected into the O_2 stream, with the discharge on, at a rate of about 2.4×10^{-6} mole/sec. Most of the organic material was collected in the first trap, using liquid nitrogen as coolant. Unreacted TME was removed by careful distillation, under vacuum, and a colorless, viscous liquid remained in the trap. This material readily liberated I_2 from KI and had ir and nmr spectra identical with those of 2, synthesized by photochemical oxidation of TME.¹⁶ These spectra also closely matched those recently reported by Foote, *et al.*¹⁷ The mass spectrum of 2 was also recorded (Perkin-Elmer-Hitachi mass spectrometer), the sample being introduced at room temperature. At a chamber voltage of 18 eV, the base peak occurs at mass number 82 (cleavage of H_2O_2) the abundance of the molecular ion (mass number 116) being *much* less than 0.1% of this, as expected for an unstable hydroperoxide. The mass spectrum alone does not provide definite proof of structure.

The hydroperoxide, 2, was also reduced to 2,3-dimethyl-1-buten-3-ol (5), in 100% yield, using tri-

(16) G. O. Schenck and K-H. Schulte-Elte, *Ann.*, 618, 185 (1958).

(17) C. S. Foote, S. Wexler, W. Ando, and R. Higgins, *J. Amer. Chem. Soc.*, 90, 975 (1968). These authors did not report any absorption corresponding to the C-H stretching vibration in the terminal olefinic CH_2 group of 2. This is observed at 3095 cm^{-1} in dilute CCl_4 solution and at 3105 cm^{-1} in the gas phase. Also, the absorption of 5 at 1105 cm^{-1} was not reported.

(15) F. C. Fehsenfeld, K. M. Evenson, and H. P. Broida, *Rev. Sci. Instr.*, 36, 294 (1965).

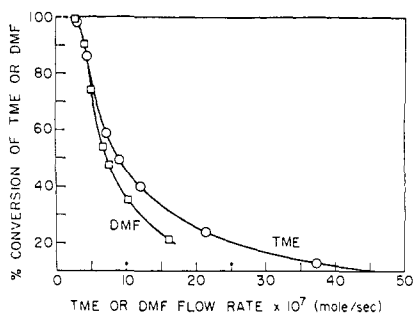
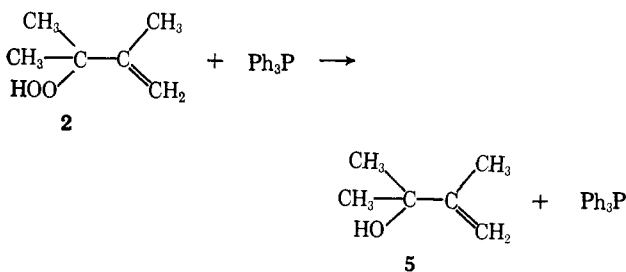


Figure 2. The dependence of conversion of TME and DMF on the TME and DMF flow rates.

phenylphosphine.¹⁶ The alcohol, **5**, was identified by its ir spectrum.¹⁷



The products from the reaction of TME, collected in the first trap, were quantitatively analyzed by glpc. Control experiments showed that pure **2**, injected onto a column at 55–60° (injector at 75°), gave a single peak on the chromatogram. The compound responsible for this peak was collected, using a chromatograph with a catharometer detector, and proved to be **2** by ir and nmr spectroscopy. Reinjection of the collected liquid gave the same single peak. Thus the analysis of **2** by glpc, caused no decomposition. However, at column temperature above 70°, the quantity of **2** reaching the detector was much reduced, considerable background was recorded on the chromatogram, and a second peak developed, with an appearance time identical with that of **5**, under various conditions.

In the initial experiments, about 50% of the injected TME was consumed, but glpc analysis of the trapped material confirmed the presence of only unreacted TME and **2**. Pure **2** was obtained directly by cooling the first trap to –45° with a Dry Ice–acetone bath. At this temperature, **2** was efficiently trapped, but TME passed through and was collected in the subsequent traps cooled in liquid nitrogen. No other products were detected by glpc analysis of the material.

The microsampling valve, maintained at a temperature of 60°, was used to measure the TME concentration in the oxygen stream. The dependence of the percentage conversion of TME to **2** on the TME flow rate is given in Figure 2. The conversion was calculated from the TME peak areas a , on the glpc recording, with the discharge on and off, using the equation

$$\text{per cent conversion} = 100(a_{\text{OFF}} - a_{\text{ON}})/a_{\text{OFF}}$$

It is clear from Figure 2 that almost 100% conversion of the TME occurs at low flow rates.

When the gas stream was passed through the 10-m ir cell, with the discharge off, the recorded ir spectrum was essentially identical with that of TME in CCl₄

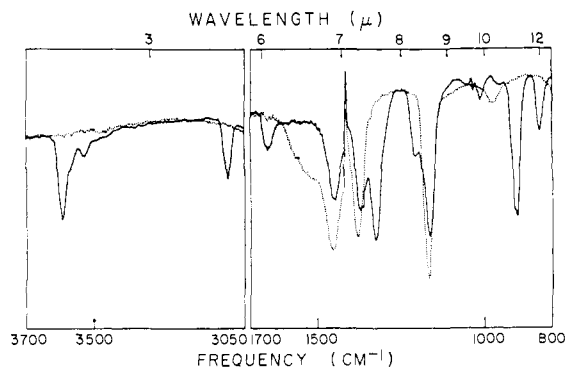


Figure 3. Gas phase infrared spectra of TME (· · ·) and its reaction product (—) with singlet oxygen (¹Δ_g).

and of TME vapor in the absence of O₂. This indicates that O₂(³Σ_g⁻) and TME did not react, under the conditions used. With the discharge on, and the TME flow rate so low that all the TME was consumed, a different ir spectrum was recorded. This was identical with that of pure **2**, obtained by passing its vapor through the reaction vessel and ir cell, with the discharge off. This is *direct* evidence that O₂(¹Δ_g) and TME react to produce **2** in the gas phase. Portions of the ir spectra are shown in Figure 3. Analysis of the condensate in the traps by glpc showed that **2** was the sole product, even when all the injected TME was consumed.

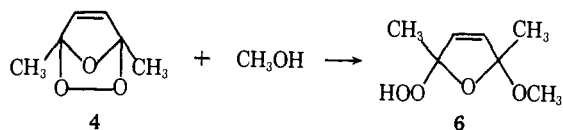
Samples of the gas stream were also analyzed by glpc, using the Carle valve. With the discharge off, a single peak, produced by TME, was obtained on the chromatogram. On sampling with the discharge on, the TME peak was much smaller and three new peaks appeared, *none* of which corresponded to **2**. However, the material condensed in the traps consisted only of TME and **2**. The higher the temperature of the valve, the more pronounced the additional peaks became. The hydroperoxide, **2**, could not be detected in the gas stream using the sampling valve, although this was the only product collected in the traps, and the only product detected in the gas stream by ir spectroscopy. However, the sampling technique gave very reproducible peak areas for the TME, with the discharge either on or off. The sampling valve, whose temperature was maintained at 60°, was used exclusively for determining the TME content of the gas stream. We conclude that, at this temperature, **2** is stable during glpc analysis with the columns used, but apparently it, or some intermediate precursor, decomposes in the metal sampling valve.

These results unambiguously establish that TME and O₂(¹Δ_g) do react in the gas phase. The only product of the reaction of O₂(¹Δ_g) with TME is **2**, and, as this was obtained pure in such high yields, a definitive identification was possible. No other products were detected by gas phase ir spectroscopy or by glpc analysis of trapped reaction materials. In particular, no acetone was evident, confirming the absence of reactions with O(³P) and O₃.

2,5-Dimethylfuran. In the sensitized photochemical oxidation of DMF (**3**), reaction with O₂(¹Δ_g) is believed to give the ozonide, **4**, which is unstable at room temperature.¹⁸ When the photochemical reaction is per-

(18) C. S. Foote, M. T. Wuesthoff, S. Wexler, I. G. Burstain, R.

formed in methanol the isolated product is the hydroperoxide, **6**.¹⁸ For our investigation in the gas phase,



the procedures were the same as those used for TME. The vapor of DMF was injected and the exit gases from the reaction chamber were analyzed by glpc, using the sampling valve. The chromatogram peak for the DMF was very reproducible and became much smaller when the discharge was switched on. When the discharge was operating, *no products* could be detected in the gas stream by glpc analysis. The dependence of DMF conversion on the DMF injection rate is shown in Figure 2.

With the discharge off, the vapor of DMF was passed through the 10-m cell and its ir spectrum was identical with that recorded in the absence of O₂. With the discharge operating, and a low DMF injection rate, for which glpc analysis of the gas stream indicated 100% reaction of the DMF, a completely different ir spectrum was recorded. Portions of these spectra are shown in Figure 4. The product spectrum showed no absorbance characteristic of carbonyl or hydroxyl groups, and confirmed the total reaction of the DMF. Ozonides in CCl₄ solution show a weak, but characteristic, absorption at 840–860 cm⁻¹.¹⁹ The product from the reaction of DMF shows weak absorptions at 862 and 869 cm⁻¹. Under conditions where 100% of the DMF reacted, a colorless crystalline solid collected on the walls of the first trap, which was immersed in liquid nitrogen. On warming these crystals to temperatures above -30° in the presence of O₂, melting occurred with considerable frothing, eventually producing a resinous material. A sample of the colorless crystals was warmed in an evacuated bulb. A mass spectrometric examination showed that the gas given off during the decomposition was oxygen. The crystals also readily oxidized KI to I₂.

The colorless crystalline material appeared similar to that obtained by sensitized photochemical oxidation of DMF in benzene-petroleum ether at -24°, which is believed to be **4**.¹⁸ Excess methanol chilled to -45° was added to the crystals in the trap at -80°, in an argon atmosphere. After slowly warming to room temperature and removing the solvent, the residual syrup was examined. Comparison of its ir spectrum with that of pure **6** indicated the presence of **6**, but the sample was not sufficiently pure or stable to isolate it in crystalline form. Substantial quantities of polymeric materials were produced.

The colorless crystals from the reaction of O₂(¹Δ_g) and DMF were treated with Ph₃P in ether at -45°,¹⁸ and gave a 72% yield of *trans*-1,2-diacetylene, based on the DMF consumed. The *trans*-1,2-diacetylene had mp 76° (lit.¹⁸ mp 78°) and readily formed the bis-2,4-dinitrophenylhydrazone, which was purified by recrystallization from pyridine, mp 277° dec (lit. mp 276–278°,²⁰ 284–286°¹⁸). The identifica-

Denny, G. O. Schenck, and K-H. Schulte-Elte, *Tetrahedron*, **23**, 2583 (1967).

(19) P. R. Story, *et al.*, private communication of unpublished results.

(20) J. Levisalles, *Bull. Soc. Chim. France*, 997 (1957).

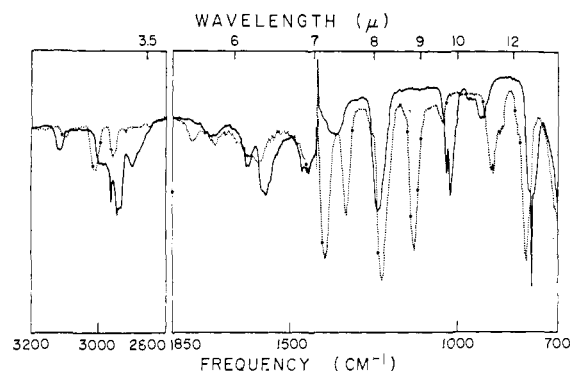


Figure 4. Gas phase infrared spectra of DMF (—) and its reaction product (· · ·) with singlet oxygen (¹Δ_g).

tion was confirmed by the ir spectrum (CCl₄, ν 1680 cm⁻¹, α,β-unsaturated ketone) and nmr spectrum (CDCl₃, singlets at τ 3.20 and 7.61 with intensities in the ratio 1:3). The ozonide, **4**, should give the *cis* isomer but this apparently rearranges to the more stable *trans* form during isolation.²⁰

A sample of the colorless crystals, suspected to be **4**, was dissolved in CDCl₃ at -50°, in an argon atmosphere. The solution was rapidly transferred to a chilled nmr tube, previously filled with argon, and the nmr spectrum of the solution recorded at -50°. The spectrum consisted only of two sharp singlets at τ 3.48 and 8.10 with intensities in the ratio 1:3, respectively. The nmr spectrum of DMF under identical conditions also consisted of two sharp singlets but at τ 4.11 and 7.76, with intensities in the ratio 1:3, respectively. The *cis*-olefinic protons in **4** have a very similar environment to those in ascaridole, which are responsible for absorptions at τ 3.53 and 3.58 in the nmr spectrum in CDCl₃ at room temperature.²¹ The product from the sensitized photooxidation of DMF, in methanol at low temperatures, which is considered to be the ozonide, **4**, has an nmr spectrum in methanol consisting of two singlets at τ 3.56 and 8.28.²² The intensities are in the expected 1:3 ratio.

Although the ir technique detected the formation of the product from O₂(¹Δ_g) and DMF, no products were detected in the oxygen stream by glpc analysis. It seems very probable that the ozonide, **4**, would decompose in the metal sampling valve and apparently the decomposition products are not particularly volatile, and do not include DMF itself.

The ease with which the gas phase ir spectrum of the product from O₂(¹Δ_g) and DMF could be recorded and the ease with which the colorless crystals, collected in the trap, dissolved in organic solvents at -50°, suggest that the ozonide, **4**, does not polymerize readily in the gas phase at 22° or in the solid state at -50°. However, on warming the solid above -30°, oxygen is evolved and polymeric materials are produced. The gas phase ir spectrum and the absence of any peaks on the glpc recording, apart from that corresponding to DMF, strongly suggests that the reaction between DMF and O₂(¹Δ_g) gives only the ozonide, **4**, and that this product can be formed in about 100% yield at low DMF injection rates.

(21) Varian Associates NMR Spectra Catalog, Palo Alto, Calif., 1962.

(22) C. S. Foote, *et al.*, private communication of unpublished results.

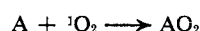
Table I. Rate Constants for the Reaction of $O_2(^1\Delta_g)$ with TME and DMF at Various Injection Rates

[TME], mole/l.	k_{TME} , l./mole sec	[DMF], mole/l.	k_{DMF} , l./mole sec	k_{DMF}^* , ^a l./mole sec
2.0×10^{-6}	3.7×10^5	1.2×10^{-6}	1.2×10^6	4.8×10^5
3.4×10^{-6}	2.4×10^5	1.6×10^{-6}	1.7×10^6	3.5×10^5
4.2×10^{-6}	1.7×10^5	1.7×10^{-6}	1.0×10^6	3.5×10^5
5.6×10^{-6}	1.5×10^5	2.0×10^{-6}	1.5×10^6	4.4×10^5
9.9×10^{-6}	1.1×10^5	2.1×10^{-6}	1.6×10^6	2.3×10^5
17.3×10^{-6}	0.9×10^5			

^a k_{DMF}^* was calculated using the $[^1O_2]_0$ obtained from the TME reaction.

Kinetics. Tetramethylethylene. As explained earlier, the spherical reactor had to be replaced by a linear tube so that the time of contact of the injected TME or DMF with the $O_2(^1\Delta_g)$ could be accurately measured. The contact time, t , was determined using the equation $t = \text{reactor volume between injection and deactivation sites}/\text{oxygen volume flow rate}$.

Reaction of TME or DMF with $O_2(^1\Delta_g)$ can be represented by the equation



Assuming that this is a simple bimolecular reaction

$$\frac{-d[A]}{dt} = k[A][^1O_2]$$

Integration gives

$$kt = \frac{2.303}{[^1O_2]_0 - [A]_0} \log \left(\frac{[A]_0[^1O_2]_t}{[A]_t[^1O_2]_0} \right)$$

where k is the bimolecular rate constant, t the contact time and the subscripts 0 and t refer to concentrations at time zero and t . This equation was used to determine values of k for TME and DMF.

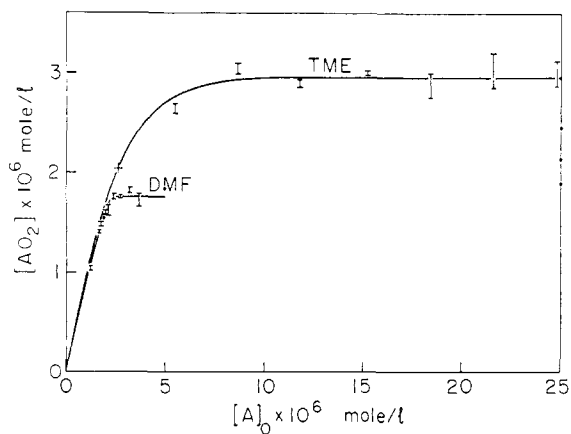


Figure 5. Dependence of A consumed on the initial concentration of A, for TME and DMF.

To calculate k , concentrations of A in the oxygen stream were measured by glpc analysis using the micro-sampling valve. Calibration curves relating the concentration of A to its glpc peak area were prepared.

$$[A]_0 \sim a_{OFF} \quad (\text{discharge off})$$

$$[A]_t \sim a_{ON} \quad (\text{discharge on})$$

The initial concentration of $O_2(^1\Delta_g)$ was measured by examining the dependence of A consumed on its injection rate. Assuming a simple bimolecular reaction

between A and $O_2(^1\Delta_g)$, then

$$[^1O_2]_0 - [^1O_2]_t = [A]_0 - [A]_t \sim (a_{OFF} - a_{ON})$$

The results are shown in Figure 5. If sufficient A is present, the amount consumed becomes independent of the injection rate, as shown by the occurrence of the plateaus in Figure 5. This condition corresponds to complete removal of $O_2(^1\Delta_g)$ by reaction with A within time t . Thus

$$[^1O_2]_0 \sim (a_{OFF} - a_{ON})_{max}$$

$$[^1O_2]_t \sim (a_{OFF} - a_{ON})_{max} - (a_{OFF} - a_{ON})$$

Values of a_{OFF} and a_{ON} were measured at increasing injection rates of A until the maximum value of $(a_{OFF} - a_{ON})$ was found. Calculations of k were carried out on data for which $(a_{OFF} - a_{ON})$ was well below this limiting value so that reaction of $O_2(^1\Delta_g)$ was incomplete. Rate constants, determined under various conditions, are given in Table I and are shown in Figure 6. These results indicate that k_{TME} reaches a limiting value of $(1.0 \pm 0.5) \times 10^5$ l. mole⁻¹ sec⁻¹, at high concentrations of TME. The data given in Figure 6 and Table I were not obtained from Figure 5 which only represents a typical gas titration curve.

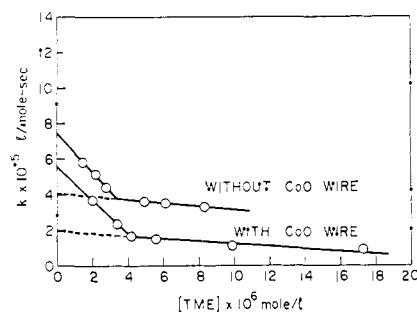
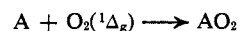


Figure 6. Dependence of k_{TME} on the initial substrate concentration and on the deactivation effect of the CoO wire on $O_2(^1\Delta_g)$.

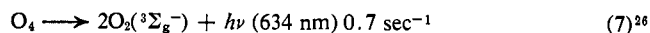
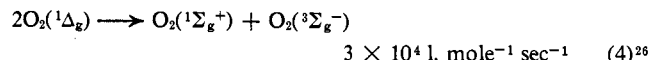
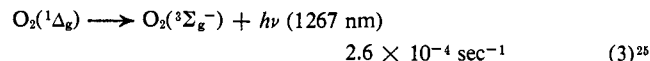
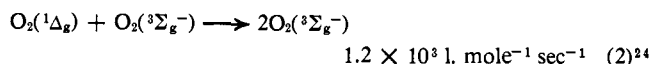
The kinetic analysis described is valid if A and $O_2(^1\Delta_g)$ are consumed only by the reaction



We have shown earlier that both the gas stream and the trapped material from the reaction of TME contained only one product. There was no evidence for any removal of the organic reactant by reaction with $O(^3P)$ or O_3 . In addition, TME did not react with $O_2(^3\Sigma_g^-)$ under our experimental conditions, since a_{OFF} was independent of contact time with $O_2(^3\Sigma_g^-)$. Gas phase ir spectroscopy also indicated that no removal of TME occurred when the discharge was off. Furthermore, the addition of sufficient water vapor

above the reaction zone to deactivate any remaining $O_2(^1\Sigma_g^+)$ caused no detectable change in k_{TME} . This indicated that $O_2(^1\Sigma_g^+)$ does not contribute significantly to the reaction of singlet oxygen with TME and that the primary oxygen reactant is $O_2(^1\Delta_g)$.

In addition to reaction with A, there are several known alternative reactions of $O_2(^1\Delta_g)$, which could result in its deactivation in this system. These are listed, with the appropriate rate constants.



Of these reactions which decrease the concentration of $O_2(^1\Delta_g)$ available for reaction with TME, reactions 1, 2, and 4 should be the most significant. The value of $[^1O_2]_0$, determined by injecting TME at increasing concentrations until the product concentration became constant would be 20% too low because of reactions 1, 2, and 4. This is based on the concentrations of $O_2(^1\Delta_g)$, $O_2(^3\Sigma_g^-)$, and TME being 3×10^{-6} , 3×10^{-4} , and 2.5×10^{-5} mole/l., respectively, and the rate constant for reaction of $O_2(^1\Delta_g)$ and TME being 1.0×10^5 l. mole⁻¹ sec⁻¹. At an initial TME concentration of 5×10^{-6} mole/l. $[^1O_2]_i$ as measured by glpc will be only 55% of the true value. Therefore, in the calculation of the rate constant the values of $[^1O_2]_0$ and $[^1O_2]_i$ should be 4×10^{-6} and 2×10^{-6} mole/l., rather than say 3×10^{-6} and 1×10^{-6} mole/l. If these corrected concentrations are used to recalculate the rate constant, they only cause a slight increase in k_{TME} . This could not be greater than double the experimental value of 1.0×10^5 l. mole⁻¹ sec⁻¹, and the discrepancy would be less at higher initial TME concentrations. For this reason, $k_{TME} = (1.0 \pm 0.5) \times 10^5$ l. mole⁻¹ sec⁻¹ is a reliable measure of the reaction rate constant. This would correspond to only one reaction for every 1×10^6 collisions between $O_2(^1\Delta_g)$ and TME. However, this is 100 times faster than the deactivation of $O_2(^1\Delta_g)$ by collision with $O_2(^3\Sigma_g^-)$. This rate of reaction is consistent with the low reactivity which has been observed for $O_2(^1\Delta_g)$ in solution. There is no doubt that k_{TME} is considerably less than the estimated value of 10^8 l. mole⁻¹ sec⁻¹, reported by Ogryzlo, *et al.*²⁶

The possibility also arises that the experimentally determined values of $[^1O_2]_0$ and $[^1O_2]_i$ could be too low because of collisional deactivation of $O_2(^1\Delta_g)$ by TME and also by its oxidation product, 2. At a total pressure of 1 Torr, it was possible to inject TME and suffi-

(23) Experimentally determined for this apparatus.

(24) F. D. Findlay, C. J. Fortin, and D. R. Snelling, *Chem. Phys. Letters*, **3**, 204 (1969).

(25) R. M. Badger, A. C. Weight, and R. F. Whitlock, *J. Chem. Phys.*, **43**, 4345 (1965).

(26) S. J. Arnold, M. Kubo, and E. A. Ogryzlo, "Oxidation of Organic Compounds," *Advances in Chemistry Series*, No. 77, American Chemical Society, Washington, D. C., 1968, p 133.

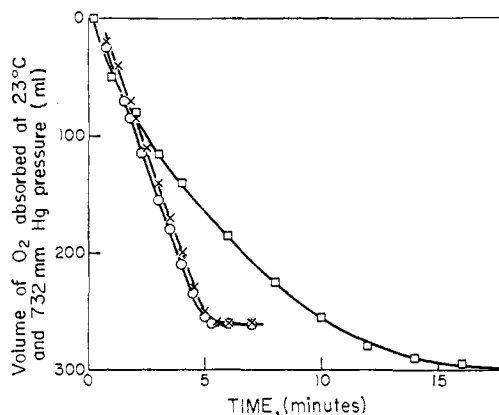


Figure 7. Rate of oxygen absorption during photooxidation of TME in methanol, sensitized by methylene blue perchlorate: O, 1.1×10^{-2} mole of TME in 170 ml of CH_2OH ; X, 1.1×10^{-2} mole of TME and 6.6×10^{-2} mole of 2 in 170 ml of CH_2OH ; □, 1.3×10^{-2} mole of TME and 1.8×10^{-2} mole of 1,4-diazabicyclo[2.2.2]octane in 170 ml of CH_2OH .

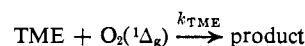
cient of the less volatile 2 into the linear reactor, so that the concentration of 2 was double that previously found in the rate constant measurements. With or without added 2, $[^1O_2]_0$, determined by the plateau method, was $1.7 \pm 0.2 \times 10^{-6}$ mole/l., indicating negligible deactivation of $O_2(^1\Delta_g)$ by 2.

Investigations of the kinetics of oxygen consumption in the photooxidation of TME in solution in methanol, sensitized by methylene blue perchlorate, also showed no evidence of any deactivation of $O_2(^1\Delta_g)$ by 2. The reaction was found to be strictly zero order, probably because the rate-controlling step was dissolution of the O_2 in the methanol

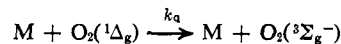
rate of O_2 consumption =

$$\text{rate of formation of } O_2(^1\Delta_g) \times \frac{k_{TME}[TME]}{k_{TME}[TME] + k_q[M]}$$

where



and



A zero-order reaction indicates that $k_{TME}[TME] \gg k_q[M]$.

The reaction order and rate of oxygen consumption were unaffected by addition of 2 to give an initial concentration six times greater than the initial TME concentration (Figure 7). However, a drastic decrease in rate and a non-zero order reaction were found on addition of 1,4-diazabicyclo[2.2.2]octane, to give a concentration about equal to the initial TME concentration. Ouannes and Wilson²⁷ have recently reported that the diazabicyclooctane actually quenches $O_2(^1\Delta_g)$ in solution and in the gas phase.

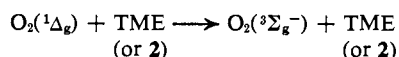
Any collisional deactivation of $O_2(^1\Delta_g)$ by TME would not be detectable in the experiments described. However, deactivation by other gases could be studied. Injection of 2,3-dimethylbutane, 2,3-dimethyl-1-butene,

(27) C. Ouannes and T. Wilson, *J. Amer. Chem. Soc.*, **90**, 6527 (1968).

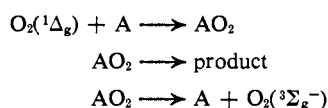
or isobutene, at concentrations equal to the largest TME concentration required to give a plateau for $(a_{\text{OFF}} - a_{\text{ON}})_{\text{max}}$ gave no change in this plateau and therefore no change in $[\text{}^1\text{O}_2]_0$ (Figure 5). These compounds did not react with $\text{O}_2(^1\Delta_g)$ under the experimental conditions and the constancy of $[\text{}^1\text{O}_2]_0$ indicated that collisional deactivation of $\text{O}_2(^1\Delta_g)$ by these inert hydrocarbons was negligible. Considering the similarities in structure between these compounds and TME, it seems reasonable to assume that collisional deactivation of $\text{O}_2(^1\Delta_g)$ by TME is insignificant.

When the initial TME concentration exceeds $[\text{}^1\text{O}_2]_0$, the measured value of k_{TME} is essentially constant at 1.0×10^5 l. mole⁻¹ sec⁻¹ (Figure 6). However, at low TME concentrations a definite increase in k_{TME} was found. This probably results because the values of $[\text{}^1\text{O}_2]_0$ and $[\text{}^1\text{O}_2]_t$, used in the calculations, are too low. At high TME concentrations, errors in $[\text{}^1\text{O}_2]_0$ and $[\text{}^1\text{O}_2]_t$ tend to cancel in the term $[\text{}^1\text{O}_2]_0/[\text{}^1\text{O}_2]_t$ and do not markedly affect k_{TME} because the value of $[\text{A}]_0 - [\text{}^1\text{O}_2]_0$ is determined largely by $[\text{A}]_0$. The opposite applies when $[\text{}^1\text{O}_2]_0$ exceeds $[\text{A}]_0$, and calculations using a low value of $[\text{}^1\text{O}_2]_0$ give larger values of k_{TME} .

The results demonstrate that losses of $\text{O}_2(^1\Delta_g)$, by processes other than reaction with TME, do occur. These may be: (1) collisional deactivation of $\text{O}_2(^1\Delta_g)$ by $\text{O}_2(^3\Sigma_g^-)$ with some contributions from reactions 1 and 4, (2) collisional deactivation of $\text{O}_2(^1\Delta_g)$ by TME or the hydroperoxide 2. (If it is assumed that TME would behave similarly to the related hydrocarbons, 2,3-dimethyl-1-butene, 2,3-dimethylbutane, and isobutene, then the maximum rate constant for the deactivation process



would not be much greater than 10^4 l. mole⁻¹ sec⁻¹ or the deactivation would have been measurable; this is based on an experimental accuracy of $\pm 5\%$ in measuring $[\text{}^1\text{O}_2]_0$) (3) loss of $\text{O}_2(^1\Delta_g)$ by reversible addition to TME



This mode of deactivation could not occur with the inert hydrocarbons used as models for TME since these were shown not to react with $\text{O}_2(^1\Delta_g)$. In the case of TME, the molecule AO_2 may be a dioxetane, and this may be a collisionally stabilized or a hot molecule. While evidence for the occurrence of dioxetane intermediates in reactions of $\text{O}_2(^1\Delta_g)$ has recently been reported,²⁸ we feel that it is not yet unequivocal and we will not speculate further on this point.

If such an intermediate occurs as a hot molecule, then it should be possible to stabilize it by collisional deactivation, thereby increasing the concentration of 2. This premise was tested by running a competitive reaction between TME and 2,3-dimethyl-1-butene, the latter being used as the deactivating molecule. This was carried out at low concentration of TME where the unusually high value of k_{TME} occurs. The results indicated a 15% decrease in the value of k_{TME} . The

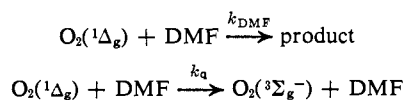
(28) W. Fenical, D. R. Kearns, and P. Radlick, *J. Amer. Chem. Soc.*, **91**, 3396 (1969).

2,3-dimethyl-1-butene did not bring k_{TME} down to a constant value of 1×10^5 l. mole⁻¹ sec⁻¹. However, it was not expected to be as satisfactory a stabilizer for the AO_2 intermediate as TME. Although TME does not appear to deactivate singlet oxygen to any great extent, it apparently can stabilize the intermediate and increase the production of the TME hydroperoxide.

Therefore, it may be concluded that the most probable cause for the high values of k_{TME} at low concentrations of TME is the decrease in the stabilization of the AO_2 intermediate by TME and the competition from reactions 2 and 4.

Dimethylfuran. Values of the rate constant for the reaction between $\text{O}_2(^1\Delta_g)$ and 2,5-dimethylfuran (DMF) were determined by the same procedure used for TME. Values of k_{DMF} were essentially independent of the initial DMF concentration and equal to $(1.4 \pm 0.4) \times 10^6$ l. mole⁻¹ sec⁻¹ (Table I). However, significant differences were found in the values of $(a_{\text{OFF}} - a_{\text{ON}})_{\text{max}}$ determined using DMF and TME. The initial concentration of $\text{O}_2(^1\Delta_g)$, determined by the plateau method using DMF, was always about 50% of that measured using TME (Figure 5). This was confirmed in one experiment where TME and then DMF were injected, while all the conditions of oxygen flow, pressure, and discharge operation were maintained constant. This was direct evidence that DMF can remove $\text{O}_2(^1\Delta_g)$ by some process which does not consume DMF. Because the values of $[\text{}^1\text{O}_2]_0$, used to calculate k_{DMF} , were about 50% too low, the rate constants were recalculated using $[\text{}^1\text{O}_2]_0$ determined with TME, and $[\text{}^1\text{O}_2]_t = (a_{\text{OFF}} - a_{\text{ON}})_{\text{max}}^{\text{TME}} - (a_{\text{OFF}} - a_{\text{ON}})^{\text{DMF}}$. The recalculated value, k_{DMF}^* , was $(3.7 \pm 1.4) \times 10^6$ l. mole⁻¹ sec⁻¹ (Table I). In solution, $k_{\text{DMF}}/k_{\text{TME}}$ has been found to equal 2.4^{4,29} so that the value $k_{\text{DMF}}^*/k_{\text{TME}} = 3.7$, in the gas phase, seems reasonable. However, because of the uncertainty in the value of $[\text{}^1\text{O}_2]_t$, k_{DMF}^* can only be regarded as an estimate.

Because DMF is more reactive toward $\text{O}_2(^1\Delta_g)$ than TME, collisional deactivation of $\text{O}_2(^1\Delta_g)$ by $\text{O}_2(^3\Sigma_g^-)$ is negligible in the DMF experiments. If the significant losses of $\text{O}_2(^1\Delta_g)$, which do not result in loss of DMF, are caused by a reversible addition, then the ozonide adduct, 4, could be a hot molecule. However, this does not appear to be the case since the DMF plateau was unaffected by the simultaneous injection of DMF with 2,3-dimethyl-1-butene at a concentration equal to that of the DMF. As in the case of TME, reversible addition of $\text{O}_2(^1\Delta_g)$ to DMF and collisional deactivation of $\text{O}_2(^1\Delta_g)$ by DMF cannot be distinguished. However, if the reactions can be represented by



Then $k_q \approx k_{\text{DMF}}$, since the DMF plateau value, $(a_{\text{OFF}} - a_{\text{ON}})_{\text{max}}^{\text{DMF}}$, is about 50% of the TME plateau value, $(a_{\text{OFF}} - a_{\text{ON}})_{\text{max}}^{\text{TME}}$.

Experiments were conducted in which DMF and TME were injected at known concentrations, mixed and allowed to compete for the available $\text{O}_2(^1\Delta_g)$. The result gave $k_{\text{DMF}}/k_{\text{TME}} > 10$. It was difficult to measure accurately the small change in the TME

(29) We have confirmed that DMF is consumed 2.5 times faster than TME in the rose bengal sensitized photooxidation in methanol.

concentration occurring for almost complete removal of the DMF. If k_{DMF}^* is not in error then the value of $k_{\text{DMF}}/k_{\text{TME}} > 10$ may be the result of the adduct from TME and $\text{O}_2(^1\Delta_g)$ transferring oxygen to DMF, to give the ozonide, 4, and regenerating TME. If this is the case, it will greatly complicate the determination of competitive rate constants in the gas phase. Such a study is now underway.

In conclusion we should note that the determination of the absolute rate constant for the reaction between TME and $\text{O}_2(^1\Delta_g)$ is particularly relevant to processes dealing with air pollution. TME is widely employed as a "typical" highly reactive internally double bonded olefin in smog chamber studies. For example, it was employed recently by Bufalini and Altshuller in their studies of the photooxidation of nitric oxide-olefin mixtures.³⁰ Our value of the rate constant for the reaction of $\text{O}_2(^1\Delta_g)$ with TME to form the allylic hydroperoxide can be compared to the rate of the reaction between ozone and TME, determined by Vrbaski and Cvetanovic,³¹ $1.0 \times 10^5 \text{ l. mole}^{-1} \text{ sec}^{-1}$ vs. $1.8 \times 10^4 \text{ l. mole}^{-1} \text{ sec}^{-1}$.³²

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Acknowledgment. The authors wish to acknowledge helpful discussions with Drs. C. S. Foote, P. R. Story, and R. P. Wayne. One of us, W. S. G., acknowledges an Air Pollution Special Postdoctoral Fellowship from the Consumer Protection and Environmental Health Service, National Air Pollution Control Administration. This research was supported by Grants AP 00109 and AP 00771 from the Research Grants Branch, National Air Pollution Control Administration, Consumer Protection and Environmental Health Service, U. S. Public Health Service.

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(32) After the submission of this paper, an article appeared by Herron and Huie [*J. Chem. Phys.*, **51**, 4164 (1969)] in which they quoted a value for k_{TME} of $1.0 \times 10^6 \text{ l. mole}^{-1} \text{ sec}^{-1}$. Their value was calculated using a singlet oxygen concentration which had been determined by assuming that in the reaction of singlet oxygen with DMF, the singlet oxygen was primarily removed by chemical reaction with DMF. If, however, a correction is made for the disappearance of 50% of the singlet oxygen by collisional deactivation with DMF, as we have found, then their value of k_{TME} is decreased by a factor of 10, bringing it into good agreement with our value of $k_{\text{TME}} = 1.0 \times 10^6 \text{ l. mole}^{-1} \text{ sec}^{-1}$.

Electrostatic Catalysis by Ionic Aggregates. I. The Ionization and Dissociation of Tritel Chloride and Hydrogen Chloride in Lithium Perchlorate-Diethyl Ether Solutions¹

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Abstract: Lithium perchlorate is shown to form with diethyl ether two crystalline etherates, a monoetherate, $\text{LiClO}_4 \cdot \text{Et}_2\text{O}$, and a dietherate, $\text{LiClO}_4 \cdot 2\text{Et}_2\text{O}$. The nmr spectra of $\text{LiClO}_4\text{-Et}_2\text{O}$ solutions show a rapidly exchanging ether solvation sphere around the lithium ion down to -100° . The shift downfield of the methylene and methyl protons of diethyl ether in lithium perchlorate-diethyl ether mixtures (hereafter LPDE) relative to pure ether can be accounted for by an average ether to lithium perchlorate ratio of 2:1 below 4.25 M and both 2:1 and 1:1 ratio above 4.25 M LiClO_4 . The molar dielectric increment, $\Delta D/\Delta C$, as determined in dilute LPDE solutions is 1.2. The ionization of triphenylmethyl chloride (hereafter TCl) was used as a sensitive probe in the study of LPDE solutions with respect to their capacity to assist ionization and sustain dissociation. Rates of exchange were monitored between TCl and $^{36}\text{Cl}^-$ under a variety of conditions and a complete kinetic analysis was carried out in terms of triphenylmethyl chloride ionization and ion recombination. The dissociation constant of TCl increases 7×10^9 -fold on going from pure ether to a 5.05 M LiClO_4 solution. The tremendous catalytic effect of LPDE solutions was also documented with respect to HCl solutions in ether.

Increased interest in reactions carried out in fused salts⁴⁻⁶ and the general lack of data on concentrated salt solutions in media of low dielectric prompted us to

study the behavior of lithium perchlorate in diethyl ether. Lithium perchlorate is very soluble in ether and at 30° solutions containing up to 6 M salt can be obtained.^{7,8} In the latter concentration region there are, on the average, 1.2 ether molecules available to solvate each lithium perchlorate. Such highly concentrated salt solutions in solvents of low dielectric have been considered by Kraus⁹ to be like fused salts with small amounts of solvent added. Our studies start with dilute

(1) This work was supported in part by the National Science Foundation (GP-5103) and in part by the donors of the Petroleum Research Fund (PRF 2043-A4), administered by the American Chemical Society.

(2) To whom inquiries should be directed.

(3) Taken in part from the Ph.D. Thesis of Richard F. Buchholz, University of Washington, 1969.

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