

ESR investigation of the photoisomerization of OCIO to ClOO in an H₂SO₄ glass: Magnetophotoselection and kinetics

F. J. Adrian, J. Bohandy, and B. F. Kim

Citation: [The Journal of Chemical Physics](#) **85**, 2692 (1986); doi: 10.1063/1.451026

View online: <http://dx.doi.org/10.1063/1.451026>

View Table of Contents: <http://scitation.aip.org/content/aip/journal/jcp/85/5?ver=pdfcov>

Published by the [AIP Publishing](#)

Articles you may be interested in

[The formation of ClOO following the photoexcitation of aqueous OCIO studied by two-color, time-resolved resonance Raman spectroscopy](#)

J. Chem. Phys. **112**, 505 (2000); 10.1063/1.480540

[Sonic spray of H₂SO₄ in a swirling heated air stream](#)

J. Acoust. Soc. Am. **68**, 1913 (1980); 10.1121/1.385159

[Nucleation in H₂SO₄–H₂O mixtures](#)

J. Chem. Phys. **67**, 5982 (1977); 10.1063/1.434781

[Paramagnetism of HydrocarbonConc. H₂SO₄ Systems](#)

J. Chem. Phys. **28**, 743 (1958); 10.1063/1.1744249

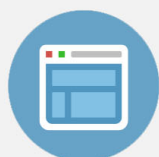
[Absorbing and Reflecting Powers of H₂SO₄ Solutions in the Far Infrared](#)

J. Chem. Phys. **4**, 413 (1936); 10.1063/1.1749871



Re-register for Table of Content Alerts

Create a profile.



Sign up today!



ESR investigation of the photoisomerization of OClO to ClOO in an H_2SO_4 glass: Magnetophotoselection and kinetics^{a)}

F. J. Adrian, J. Bohandy, and B. F. Kim

Johns Hopkins University, Applied Physics Laboratory, Laurel, Maryland 20707

(Received 17 April 1986; accepted 28 May 1986)

The photoisomerization of OClO (ClO_2) to ClOO in a sulfuric acid glass at 20 to 77 K has been reinvestigated using electron spin resonance (ESR) to observe the reactant and product and to quantitatively determine their relative concentrations. Polarized light photolysis yields a partial orientation of the remaining ClO_2 molecules (magnetophotoselection) and shows that the optical transition dipole moment lies in the molecular plane and is perpendicular to the ClO_2 rotational symmetry axis, as expected for the well known $\tilde{A}(^2A_2) \leftarrow \tilde{X}(^2B_1)$ transition of ClO_2 . Here, however, the photolysis yields only ClOO , in contrast to the gas phase where ClO is observed suggesting photodissociation. The photoisomerization kinetics are nonexponential and suggest that random variations among the ClO_2 trapping sites in the H_2SO_4 glass have a considerable effect on the probability that a photoexcited ClO_2 molecule will isomerize.

INTRODUCTION

Use of polarized light to initiate photochemical and photophysical processes in solids often orients the reactants and/or products with respect to the optical electric field (E_{opt}).¹⁻³ For paramagnetic reactants and products electron spin resonance (ESR) spectroscopy provides an especially convenient method of detecting this orientational dichroism and its relation to the internal axes of the molecule. This is because an ensemble of randomly oriented paramagnetic molecules in a host solid usually presents a broad complex ESR spectrum (powder ESR spectrum) with strong sharp-line features that correspond to those molecules which are oriented so that the magnetic field (H) is parallel to a principal magnetic axis of the molecule (principal axis lines). The changes in the relative intensities of these principal axis lines resulting from polarized light photolysis or upon rotation of a sample following such photolysis readily determines the photo-induced orientational anisotropy.⁴ Since it is usually most convenient to establish H as the reference axis of this orientational dichroism, which is readily done by setting $E_{\text{opt}} \parallel H$, this method is commonly known as magnetophotoselection,^{3,4} although it should be noted that the field does not affect the photochemical reaction per se.

This method has been extensively applied to triplet state molecules,^{3,5,6} and recently it has been extended to photochemical reactions involving doublet state paramagnetic molecules, i.e., free radicals.^{7,8} Glassy media are particularly attractive for these experiments because their high optical quality minimizes depolarization of the light by scattering. Our initial experiment was on the photodecomposition of the formyl radical in a fused silica glass⁷; this material and other substances which are solid glasses at room temperature are a promising medium for other experiments. Glasses

formed by rapid freezing of liquids seem even more promising in view of the large number of such systems. In this article we present the results of one such investigation: the photoisomerization of chlorine dioxide to the chloroperoxy radical in a sulfuric acid glass ($\text{ClO}_2 + h\nu \rightarrow \text{ClOO}$),⁹ where ClO_2 denotes the kinetically stable symmetric isomer, i.e., $\text{ClO}_2 \equiv \text{OClO}$. As these results will show, interesting data such as the polarization of the 270–510 nm optical transition of ClO_2 ,¹⁰ can be obtained even though this system presents some atypical complications. One such complication is simply that ClO_2 and ClOO have rather complicated overlapping powder ESR spectra. Another more interesting complication is that the photoisomerization of ClO_2 in an H_2SO_4 glass is found to have nonexponential kinetics.

EXPERIMENTAL

A sulfuric acid glass containing a trace of ClO_2 was prepared in a 5 mm OD ESR tube by the following procedure.⁹ KClO_3 was dissolved in concentrated H_2SO_4 and the solution diluted by adding more H_2SO_4 until the color of the solution due to the resulting ClO_2 was a very pale yellow. A typical solution contained roughly 1 mg KClO_3 in 10 ml H_2SO_4 . (As will be discussed in more detail later, the kinetics of the ClO_2 photoisomerization are complicated and the effective photolysis rate is considerably slower in more concentrated solutions of ClO_2 in H_2SO_4 .) This solution was placed in the ESR tube and subjected to several freeze-thaw cycles in liquid nitrogen to expel dissolved gases and then quickly frozen at 77 K to yield an optically clear glassy solid. Occasionally the glass devitrified during this procedure, especially while thawing, an event which often broke the ESR tube. Once frozen, however, the glasses were stable over a range of temperatures between 10 and 77 K. After the glass was formed the ESR tube was quickly transferred to the cryostat of the ESR spectrometer, where the cryostat was held at 77 K during the transfer. This cryostat, the ESR spectrometer, and the optical irradiation system have been described previously.^{7,8}

^{a)} Work supported by Naval Sea Systems Command under Contract No. 0024-85-C-5301.

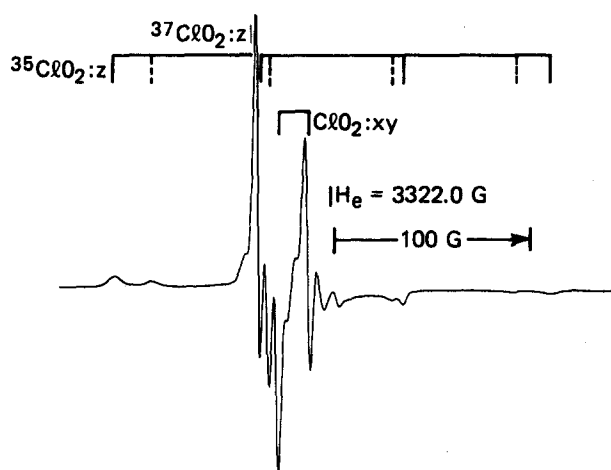


FIG. 1. ESR spectrum of ClO₂ in a sulfuric acid glass at 18 K. In this and subsequent figures H_e denotes the resonant field strength for a free electron ($g_e = 2.0023$).

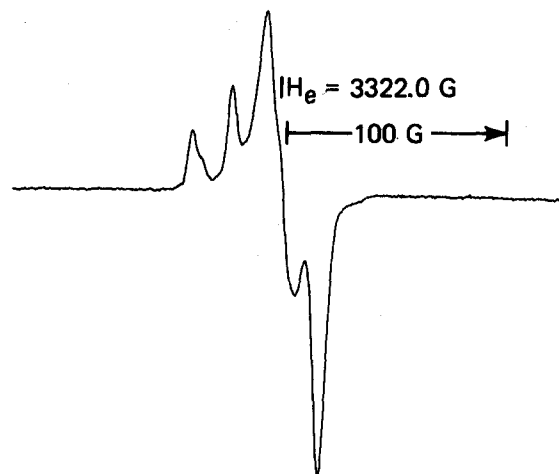


FIG. 3. ESR spectrum of ClOO produced in a sulfuric acid glass by prolonged ultraviolet photolysis of ClO₂.

RESULTS AND DISCUSSION

Magnetophotoselection in the photolysis

The ESR spectrum of ClO₂ in an H₂SO₄ glass at 18 K is shown in Fig. 1. This spectrum is quite similar to previously observed spectra of this radical in the H₂SO₄ glass⁹ and in other media.¹¹ Rotation of the sample tube by 90° about its axis did not change this spectrum, which indicates that the radicals are randomly oriented at this point.

After 15 min photolysis by light from a 200 W high pressure mercury arc lamp, which was polarized with $E_{\text{opt}} \parallel H$, and filtered to exclude ultraviolet radiation below 300 nm (Corning C. S. 0-54 filter) and nonactinic radiation in the visible and infrared regions (CuSO₄ solution filter), the ESR spectrum of the sample was as shown by the solid curve in Fig. 2. The two most readily noticed new lines in this spectrum are consistent with the presence of the ClOO radical as is readily shown by comparison with the spectrum of pure ClOO produced in a previous investigation of this pho-

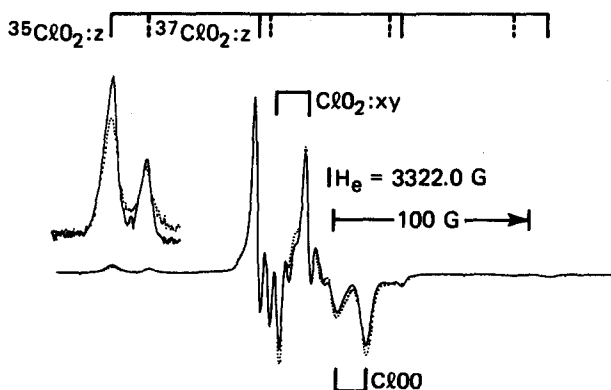


FIG. 2. Solid line: ESR spectrum at 18 K of ClO₂ and the ClOO photoproduct after 15 min photolysis with ultraviolet light polarized with its optical electric vector parallel to the magnetic field. Dotted line: ESR spectrum produced by rotating the photolyzed sample 90° about the axis perpendicular to both the direction of the light and its electric vector. The inset shows amplified traces of the lowest field line for the initial and rotated positions of the sample.

toisomerization⁹ and also observed in the present investigation, cf. Fig. 3, but only after very prolonged (~72 min) photolysis of the H₂SO₄:ClO₂ glass.

Experiments with other filters showed that radiation above approximately 400 nm does not produce isomerization even though such radiation is within the 270–510 nm absorption band of ClO₂. There is some evidence that 476.5 nm radiation photolyzes ClO₂ in the gas phase,¹² although intersystem crossing to another excited state has been suggested as an alternative explanation of the apparent predissociation observed in this case.¹³ The total intensities of the ESR spectra before and after photolysis, as obtained by double integration of the spectra shown in Figs. 1 and 2, are the same within the typical error of $\pm 5\%$ for this procedure. Thus it appears that ClO₂ is quantitatively photoisomerized to ClOO in this system, which is in interesting contrast to evidence that gas phase photolysis dissociates ClO₂ to O and ClO.^{13–15} These differences between the solid and gas phase photolysis of ClO₂ will be discussed in more detail later on.

Comparison of the original ClO₂ spectrum in Fig. 1 with that of the remaining ClO₂ and the ClOO photoproduct in Fig. 2 does reveal differences in the relative intensity decreases of the various ClO₂ lines indicating that the photoisomerization is magnetophotoselective. However, the nature of the spectrum—a composite of the rather complex ClO₂ and ClOO powder spectra—makes this procedure less definitive, and certainly less transparent, than determining the photo-induced orientational anisotropy from the spectral changes produced by rotating the sample tube about its axis. Such a 90° rotation of the tube gave the spectrum shown by the dotted curve in Fig. 2. This spectrum is clearly different from the original post-photolysis spectrum, the differences being indicative of nonrandom orientational distributions for both the ClO₂ reactant and the ClOO product. (The integrated intensities of these spectra are the same within $\pm 5\%$ showing these changes are not due to an inadvertent change in spectrometer operating conditions, and hence sensitivity during rotation of the sample.) The following analysis shows that these results can determine the orientation of the optical transition dipole moment (μ_{opt}) for the photoly-

tic transition subject to the reasonable assumption that only one transition state is involved.

The analysis of the quartet of ClO₂ lines, denoted ClO₂:z in Figs. 1 and 2, is straightforward. It is known from the ClO₂ microwave spectrum and its analysis¹⁶ that these lines are perpendicular principal axis lines, i.e., **H** is perpendicular to the ClO₂ plane, and they are a simple quartet because the Cl hyperfine splitting for this orientation is large enough to preclude significant perturbation by the Cl quadrupole interaction. Upon rotation of the sample all these lines decrease substantially except for the next to lowest field member of the group whose line is actually a composite line with additional contributions from the in-plane principal magnetic axis lines of ClO₂ and also ClOO. This decrease, which is most clearly seen in the amplified trace of the lowest field member of the quartet, shows that the optical transition leading to ClO₂ isomerization is in-plane polarized. Consequently, ClO₂ molecules oriented perpendicular to **E**_{opt} are relatively unphotolyzed, which situation is reversed, leading to the observed decrease in the perpendicular principal axis lines, as the rotation interchanges the various orientations. This conclusion agrees with theory which predicts that the subject optical transition in ClO₂ is between π electron states and thus must be in-plane polarized.^{17,18}

The determination of the in-plane orientation of μ_{opt} is considerably more complicated because it involves consideration of intensity changes in lines corresponding to the in-plane principal axes of ClO₂, whose lines considerably overlap each other and the ClOO lines. Of the various in-plane lines the most useful for our purposes are the two lines denoted ClO₂:xy in Figs. 1 and 2. These lines have the advantages of being relatively strong and relatively free of interference from the ClOO lines. Thus, our analysis, which involves simulation of the ClO₂ powder ESR spectrum and the effects on this spectrum of orientationally selective photolysis followed by sample rotation, will concentrate on these two lines.

The simulation of the spectrum followed standard procedures,¹⁹ supplemented by calculation of the Cl hyperfine-quadrupole multiplet splittings using exact diagonalization of the hyperfine energy matrix as described by Thuomas and Lund,²⁰ and also by the previously described modification of the random orientational distribution of the radicals by polarized light photolysis.^{7,8} Second order terms in the hyperfine splittings were neglected except for including an estimate of their effect on the electronic *g* factors; it was estimated that full inclusion of these second order terms would produce additional line shifts of at most ± 0.5 G which are relatively small compared to the symmetric part of the line broadening. In this calculation the symmetric broadening was represented by a Gaussian whose width between maximum and minimum slope points was 3.2 G. The best fit between the observed and simulated powder ESR spectrum of ClO₂ was obtained for the following values of the magnetic constants of this radical: $g_x = 2.0156$, $g_y = 2.0132$, $g_z = 2.0020$; and $A_x = -30.0$, $A_y = -34.0$, and $A_z = 208.3$ MHz; and $Q_x = -8.7$, $Q_y = 0.4$, and $Q_z = 8.3$ MHz, where *A* and *Q* are the ³⁵Cl hyperfine and quadrupole tensors, respectively. These *A* and *Q* values are in

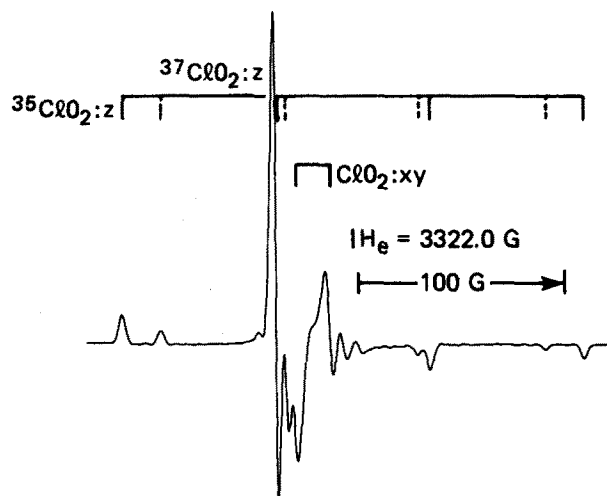


FIG. 4. Simulated powder ESR spectrum of a randomly oriented ensemble of ClO₂ molecules. The magnetic constants used are given in the text.

good agreement with the more accurate microwave spectroscopic values,¹⁶ where the microwave investigation also showed that *z* is perpendicular to the molecular plane, *y* is the *C*_{2v} symmetry axis of ClO₂, and *x* is the remaining in-plane axis. (These axis assignments are consistent with the usual ESR spectroscopic conventions, particularly for simulations of powder ESR spectra, which usually are facilitated by assigning the largest hyperfine splittings to the *z* axis. Unfortunately, they are inconsistent with optical spectroscopic notation based on the *C*_{2v} symmetry of ClO₂, which would take *z* along the rotational symmetry axis. The correspondence between these two axis conventions are $x \equiv Y$, $y \equiv Z$, and $z \equiv X$, where *X*, *Y*, and *Z* are the optical axes.) The resulting simulated spectrum is shown in Fig. 4. This spectrum agrees quite well with the observed spectrum in regard to the positions of the lines and reasonably well in regard to their intensities. The principal discrepancy in the line intensities is that the *z* axis lines in the simulated spectrum are considerably more intense relative to the in-plane lines than are their experimental counterparts. This difference might

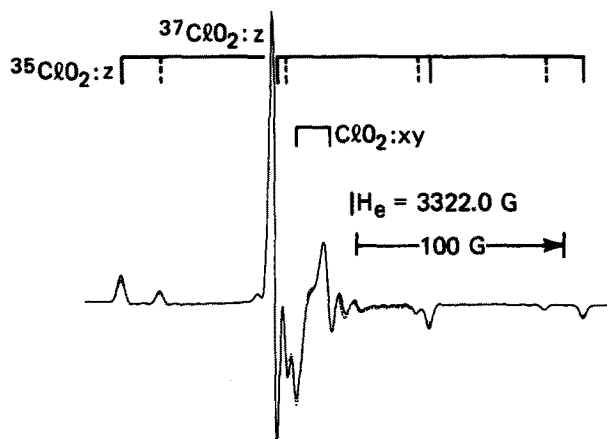


FIG. 5. Solid line: Simulated powder ESR spectrum of ClO₂ following polarized light photolysis with **E**_{opt} || **H** and μ_{opt} || **x**. Photolysis intensity and duration are such as to yield a 40° decrease in the *x* principal axes lines. Dotted line: Simulated powder ESR spectrum of ClO₂ for the foregoing photolysis followed by a 90° rotation of the sample.

be due to radical-host interactions which spread out the z component of the hyperfine splitting tensor more than the in-plane components, thereby broadening the z axis lines; there is obviously some additional broadening of the outermost lines of the z principal axis quartet in the observed spectrum. In any event, the agreement between the observed and simulated spectra seems good enough to attempt to determine the in-plane orientation of μ_{opt} by simulation of the effects on these spectra of polarized light photolysis and subsequent sample rotation.

The solid curve in Fig. 5 shows the simulated ClO₂ powder ESR spectrum produced by polarized light photolysis with $E_{\text{opt}} \parallel H$ for the case of the optical transition moment parallel to the x axis ($\mu_{\text{opt}} \parallel x$), and the dotted curve in Fig. 5 shows the simulated spectra produced by a 90° rotation of this photolyzed sample about the axis perpendicular to E_{opt} and the direction of the light. The intensity and duration of the photolysis was such as to yield a 40% intensity decrease in the x principal axis lines, whose value was empirically chosen to reproduce the observed change in the z principal axis lines upon rotating the sample 90°. As described previously^{7,8} this intensity modification is achieved by multiplying the random orientation distribution function ($\sin \theta / 4\pi$) by $\exp(-0.50 \sin^2 \theta \cos^2 \phi)$, where θ and ϕ are the polar and azimuthal angles specifying the orientation of H in the principal magnetic axis system. As shown in the Appendix, the exact orientational distribution function resulting from the 90° sample rotation is complicated and requires introduction of a third angle variable to specify the relation of the rotation axis to the magnetic field and the molecular magnetic axes. Fortunately, as also shown in the Appendix, there is a simple approximation to this distribution function, which is quite good if the photochemical reaction is less than 50% complete. This approximation can be visualized by noting that a 90° rotation of a radical which was originally oriented with the field parallel to its x principal axis ($H \parallel x$) places the field in its yz plane. Consequently, the initial photo-induced decrease in the number of $H \parallel x$ oriented radicals will now be equally shared by the $H \parallel y$ and $H \parallel z$ orientations, a situation which can be approximated by the post-rotation distribution function: $(\sin \theta / 4\pi) \exp[-0.22(\sin^2 \theta \sin^2 \phi + \cos^2 \theta)]$. A similar calculation of the simulated ESR spectra for polarized light photolysis and subsequent 90° rotation of the sample when $\mu_{\text{opt}} \parallel y$ is shown by the solid and dotted curves, respectively, in Fig. 6.

Comparison of the experimental spectra in Fig. 2 with the simulated spectra in Figs. 5 and 6 leads to the conclusion that the optical transition is x polarized, i.e., $\mu_{\text{opt}} \parallel x$. The simulated spectra for this case predict that sample rotation yields increases of 27% and 0%, respectively, for the low and high field members of the ClO₂: xy pair, in reasonably good agreement with the observed increases of 20% and 4%. On the other hand, the simulated spectra for the $\mu_{\text{opt}} \parallel y$ case predict that sample rotation will increase these lines by 65% and 39%, respectively, which strongly disagrees with experiment. Furthermore, although it is less obvious in the simulated spectra, the $\mu_{\text{opt}} \parallel y$ case predicts that sample rotation will decrease the next to lowest field member of the ClO₂: z quartet by an amount which should be observable even

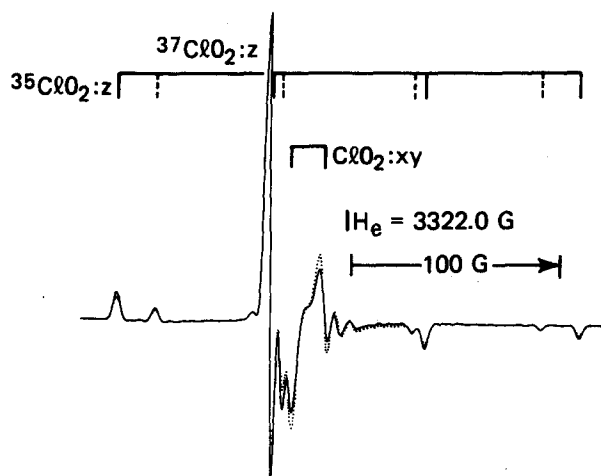


FIG. 6. Solid line: Simulated powder ESR spectrum of ClO₂ following polarized light photolysis with $E_{\text{opt}} \parallel H$ and $\mu_{\text{opt}} \parallel y$. Photolysis intensity and duration are such as to yield a 40% decrease in the y principal axes lines. Dotted line: Simulated powder ESR spectrum of ClO₂ for the foregoing photolysis followed by a 90° rotation of the sample.

though this line is complicated by being an composite of ClO₂ lines and a ClOO line, whereas the $\mu_{\text{opt}} \parallel x$ case predicts a smaller decrease that is more consistent with the observation of virtually no change in this line upon rotation. Similar predictions are made for the ³⁷Cl counterpart of this line and are somewhat more evident in Figs. 5 and 6 since this line suffers less from overlap with other lines. Here also, the predictions for the $\mu_{\text{opt}} \parallel x$ case agree better with experiment, which shows that this ³⁷Cl line is only very slightly decreased by rotation of the photolyzed sample.

This conclusion that the ClO₂ optical transition responsible for the photoisomerization is x polarized (Y or parallel polarized in optical notation) confirms that it is the $\tilde{A}(^2A_2) \leftarrow \tilde{X}(^2B_1)$ transition responsible for the 270–510 nm band of ClO₂.¹⁰ This result is of special interest because the very different results of ClO₂ photolysis in solid and gaseous media, i.e., isomerization in the former^{9,21} versus apparent dissociation in the latter,^{13–15} combined with suggestions, both theoretical¹⁸ and experimental,²² of an excited state of ClO₂ below the ²A₂ state, raise the question of whether the different photolysis results imply excitation to different excited states. Although the present determination of the polarization of the photolytic transition is not quantitative and there could be some excitation to another state, these results do show that the x -polarized $\tilde{A}(^2A_2) \leftarrow \tilde{X}(^2B_1)$ transition is the dominant one, just as it is believed to be for the gas phase photolysis.

Although the ClOO photoproduct is also partially oriented, as shown by changes in its spectrum upon rotation of the sample, this spectrum is too poorly resolved and too extensively overlapped with the ClO₂ lines to permit a detailed analysis. Furthermore, the orientational anisotropies of this photoproduct tend to be somewhat ephemeral, in particular, the orientational dichroism of the highest field ClOO line, which is clearly present in the data shown in Fig. 3, tends to decrease as the photolysis proceeds. Nonetheless, it is worth noting that the orientational dichroism observed in the highest field ClOO line indicates that this orientation of the radi-

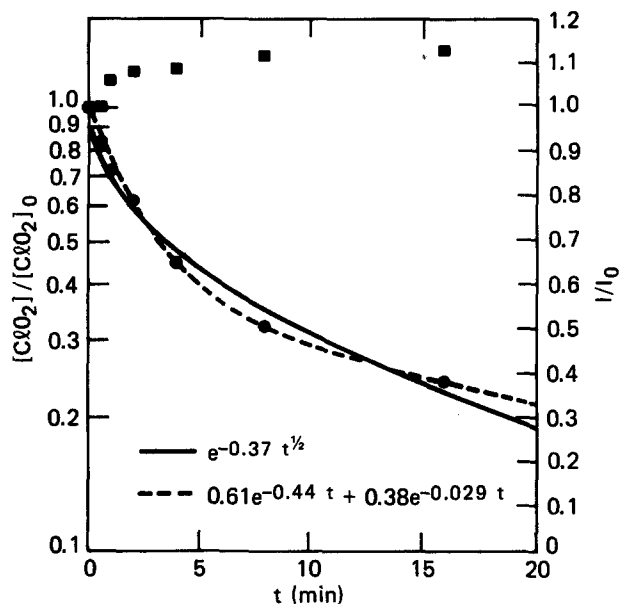


FIG. 7. ●: Fraction of ClO₂ remaining as a function of photolysis time. ■: Integrated ESR intensity relative to the initial integrated intensity as a function of photolysis time. The solid and dashed curves are empirical fits of the [ClO₂]/[ClO₂]₀ time dependence as shown in the figure.

cal is somewhat disfavored in the initial ClOO photoproduct, and that a partial analysis of the ESR spectrum of ClOO in argon at 4 K clearly shows that this line corresponds to an in-plane principal axis of the radical (the reason is that the *g* factor of this line is 1.9915, which is too far below the free electron *g* value for this axis to be perpendicular to the plane of a π radical).²³ Since the transition responsible for the ClO₂ → ClOO isomerization is in-plane polarized and an in-plane principal axis line of the photoproduct is relatively depleted there must be some reorientation of the plane of the radical during or after the isomerization.

ClO₂ photoisomerization kinetics

It was apparent from the outset that the kinetics of the ClO₂ photoisomerization did not correspond to the simple kinetics

$$\frac{d[\text{ClO}_2]}{dt} = -QI[\text{ClO}_2]; \quad [\text{ClO}_2] = [\text{ClO}_2]_0 e^{-QIt}, \quad (1)$$

where *I* is the light intensity, *Q* is the effective reaction probability per absorbed photon, and [ClO₂]₀ is the initial ClO₂ concentration. In fact, our first experiment with an H₂SO₄:ClO₂ glass containing a high concentration of ClO₂ (this glass was orange colored) required about 30 min photolysis to produce enough ClOO for its strongest ESR lines to be barely noticeable in comparison to the very intense ClO₂ spectrum, and it was not possible to reach a point where the ClO₂ and ClOO ESR intensities were comparable. As mentioned previously, only at low ClO₂ concentrations was it possible to produce the intensity changes of 25% to 50% used in the analysis of magnetophotoselective effects for reasonable photolysis times of 15 to 30 min.

Even at low ClO₂ concentrations the reaction kinetics did not obey Eq. (1). A typical result is shown in Fig. 7,

where the effective photolysis rate is clearly decreasing as the photolysis progresses. Two common explanations of this type of result are (1) The ClO₂ reactant is being replenished by photolysis of some precursor. (2) There is a back photolysis of the ClOO product to yield ClO₂. The first possibility is readily rejected because it would require a much larger increase in the integrated ESR intensity over the duration of the photolysis than the observed 12%, cf. Fig. 7. The second possibility is ruled out because ClOO does not have an optical transition at the photolysis wavelengths used²⁴ ($\lambda > 300$ nm) and, furthermore, the corresponding rate equation

$$\begin{aligned} \frac{d[\text{ClO}_2]}{dt} &= -\frac{d[\text{ClOO}]}{dt} \\ &= -Q_1 I [\text{ClO}_2] + Q_2 I [\text{ClOO}] \end{aligned} \quad (2)$$

yields the following expression for the ClO₂ concentration:

$$[\text{ClO}_2] = (Q_2 + Q_1 e^{-(Q_1 + Q_2)It}) [\text{ClO}_2]_0 / (Q_1 + Q_2). \quad (3)$$

It is not possible to fit adequately the [ClO₂] vs *t* behavior shown in Fig. 7 to an equation of the above form; for all reasonable parameters this equation tends to predict both a faster decrease in the ClO₂ concentration and a more rapid transition to the steady state than is observed.

The proposed explanation of the observed kinetic behavior is that some ClO₂ molecules are more likely than others to isomerize following photon absorption, with the differences in isomerizability being determined by random variations in the trapping sites of the ClO₂ molecules. This model can at least qualitatively account for the observed kinetic behavior in that the reaction is initially fast and then slows as the supply of easily isomerized ClO₂ molecules is depleted. Moreover, samples containing relatively large concentrations of ClO₂ are likely to be harder to photolyze because they contain enough photolysis-resistant molecules near the surface of the sample to absorb the light and prevent it from reaching photolyzable molecules in the interior. It is also possible that at high ClO₂ concentrations a relatively greater fraction of the radicals are in photolysis resistant sites. Consistent with this interpretation, as shown in Fig. 7, the data can be fit quite well by the sum of a fast and slowly decaying exponential representing those molecules which are, respectively, more and less susceptible to photolysis.

Alternatively, as also shown in Fig. 7, the data can be fit reasonably well (within 10%) by an expression of the form

$$[\text{ClO}_2] = [\text{ClO}_2]_0 \exp(-0.37t^{1/2}). \quad (4)$$

This behavior has been shown to result if the rate constant depends exponentially on some quantity such as a tunneling distance, energy barrier, etc., which is a function of some randomly distributed structural parameter of the glass.²⁵ Such behavior has been observed in a variety of processes in glassy media including hydrogen atom tunneling reactions,²⁵ relaxation processes,^{26–28} demagnetization,²⁹ and decay of “holes” burned in optical absorption bands.³⁰ The present case, however, appears to be the first example of the effect in a photo-induced reaction.

As noted previously, it appears that each photolyzed ClO₂ molecule yields ClOO with no evidence for any dissociation to ClO + O. ClO and O would be undetectable in our

experiment, because the random crystal fields of the H₂SO₄ glass acting on these orbitally degenerate species would yield a correspondingly large range of electron *g* factors and unobservably broad ESR lines, and formation of such "ESR-silent" species should result in a photo-induced decrease in the total integrated ESR intensity, whereas, as shown in Fig. 7, a small increase is actually observed. Furthermore, ClO should have been readily observable in the infrared spectroscopic investigation of the isomerization of ClOO in argon at 4 K, but was not seen there either.²¹

It thus appears that the $\tilde{A}(^2A_2) \leftarrow \tilde{X}(^2B_1)$ transition results exclusively in isomerization of ClO₂ when trapped in a solid matrix, whereas the observation of ClO in the gas phase photolysis suggests photodissociation is the dominant process there.¹³⁻¹⁵ It is unlikely that the so-called cage effect, i.e., the inability of two dissociation products to separate in a solid because of interactions with the surrounding host molecules, can fully account for this markedly different behavior. The photon energy of the radiation is sufficiently greater than the ClO₂ dissociation energy (2.5 eV)¹⁰ that at least some dissociation products should have sufficient excess energy to "melt" the glass and escape, particularly since one product is a small highly mobile atom. Such an escape process is even more likely in an argon matrix, whose melting temperature is much less than that of the H₂SO₄ glass, but photolysis of ClO₂ in Ar also failed to yield ClO.²¹

At present these apparently very different outcomes of ClO₂ photolysis in solid and gaseous media are unexplained, although there are some interesting possibilities which merit further investigation. One is suggested by gas phase experiments which indicate that the 2A_2 excited state of ClO₂ undergoes an intersystem crossing to another excited state before reacting.^{13,15} Possibly a solid environment could restrict this intersystem crossing or, more likely, provide an alternate faster reaction pathway leading to different products. Another possibility is that ClOO is formed in the gas phase photolysis but is in an excited state that immediately dissociates (a state which might be rapidly deexcited in a solid environment) or is quickly lost by various reactions that produce ClO, e.g., ClOO + ClO₂ → 2ClO + O₂.

APPENDIX

We need the orientational distribution function of an ensemble of radicals after polarized light photolysis with $\mathbf{E}_{\text{opt}} \parallel \mathbf{H}$ and a subsequent 90° rotation of the sample about the axis perpendicular to \mathbf{E}_{opt} and the direction of the light beam. In this derivation it is convenient to replace the rotation of the sample by the equivalent 90° rotation of the field \mathbf{H} .

Let the orientation of the field after rotation (\mathbf{H}') in the principal axis system of a given (reference) molecule be specified by the polar and azimuthal angles θ and ϕ , respectively. Since the rotation of this molecule about \mathbf{H}' does not change its orientation with respect to \mathbf{H}' there will be a set of molecules corresponding to this orientation, which set is generated by rotating the reference molecule about \mathbf{H}' through an angle γ ($0 < \gamma < 2\pi$).

The number of molecules at a given orientation in the rotated sample depends on how their transition dipole mo-

ments (μ_{opt}) were oriented with respect to \mathbf{E}_{opt} before the sample rotation, specifically, the number of molecules surviving the photolysis will be proportional to $\exp[-kE_{\text{opt}}^2(\mu_{\text{opt}} \cdot \mathbf{u}_H)^2]$, where \mathbf{u}_H is a unit vector in the direction of \mathbf{H} and \mathbf{E}_{opt} . To determine the orientation with respect to \mathbf{H} of the set of molecules whose orientation with respect to \mathbf{H}' is θ and ϕ , we note that the desired set of orientations is equivalent to the orientations of the reference molecule with respect to the set of fields generated by rotating \mathbf{H} through γ about \mathbf{H}' . Since \mathbf{H} is perpendicular to \mathbf{H}' and the rotation is 0 to 2π , this is just the set of all unit vectors perpendicular to \mathbf{H}' , that is,

$$\mathbf{u}_H = (\cos \theta \cos \phi \cos \lambda - \sin \phi \sin \lambda) \mathbf{i} + (\cos \theta \sin \phi \cos \lambda + \cos \phi \sin \lambda) \mathbf{j} - \sin \theta \cos \lambda \mathbf{k},$$

where \mathbf{i} , \mathbf{j} , and \mathbf{k} are unit vectors along the *x*, *y*, and *z* principal axes of the molecule.

If the optical transition is *x* polarized ($\mu_{\text{opt}} = \mu_{\text{opt}} \mathbf{i}$), then the distribution function obtained after evaluating $(\mu_{\text{opt}} \cdot \mathbf{u}_H)^2$ and simplifying with the aid of standard trigonometric identities is

$$(\sin \theta / 4\pi) \exp[-\frac{1}{2} \kappa (\sin^2 \theta \sin^2 \phi + \cos^2 \theta)] \times \exp\{-\frac{1}{2} \kappa [(\cos^2 \theta \cos^2 \phi - \sin^2 \phi) \cos 2\lambda - 2 \cos \theta \sin \phi \cos \phi \sin 2\lambda]\},$$

where $\kappa = kE_{\text{opt}}^2 \mu_{\text{opt}}^2$ ($e^{-\kappa}$ is the maximum photo-induced decrease in radical concentration which occurs for radicals oriented with their *x* axis along \mathbf{E}_{opt}) and the above expression is to be averaged over λ . The integrations over λ required to perform this average are not trivial and introduce a considerable complication into the general problem, however, if the extent of the photolysis is not too great, i.e., $e^{-\kappa} < 0.5$, then $\frac{1}{2} \kappa < 0.35$ is small enough that the averages can be carried out by expanding the λ -dependent exponential terms. The averages of the first and second terms in this expansion are unity and zero, respectively, so that the distribution function for the rotated sample is approximately $(\sin \theta / 4\pi) \exp[-\frac{1}{2} \kappa (\sin^2 \theta \sin^2 \phi + \cos^2 \theta)]$. Since the distribution function for the sample before rotation was $(\sin \theta / 4\pi) \exp[-\kappa \sin^2 \theta \cos^2 \phi]$, it is clear that sample rotation transfers the reduction in *x* line intensity equally to the *y* and *z* lines. It is readily shown that analogous behavior occurs for *y* and *z* polarized transitions.

¹G. N. Lewis and J. Bigeleisen, *J. Am. Chem. Soc.* **65**, 500 (1943).

²A. C. Albrecht, *J. Mol. Spectrosc.* **6**, 84 (1961), and references contained therein.

³M. A. El Sayed and S. Siegel, *J. Chem. Phys.* **44**, 1416 (1966).

⁴P. Kottis and R. Lefebvre, *J. Chem. Phys.* **41**, 3660 (1964), describe the method as applied to triplet state molecules; its extension to doublet state free radicals is straightforward.

⁵W. P. Chisholm, H. L. Yu, R. Murugesan, S. I. Weissman, E. F. Hellenski, and J. A. Berson, *J. Am. Chem. Soc.* **106**, 4419 (1984).

⁶S. P. McGlynn, T. Azumi, and M. Kinoshita, *Molecular Spectroscopy of the Triplet State* (Prentice-Hall, Englewood Cliffs, 1969), pp. 364-368, gives a general review of this subject.

⁷J. Bohandy, B. F. Kim, and F. J. Adrian, *Chem. Phys. Lett.* **104**, 413 (1984).

- ⁸F. J. Adrian, J. Bohandy, and B. F. Kim, *J. Chem. Phys.* **81**, 3805 (1984).
- ⁹P. W. Atkins, J. A. Brivati, N. Keen, M. C. R. Symons, and P. A. Trevalion, *J. Chem. Soc. London* **1962**, 4785; R. S. Eachus, P. R. Edwards, S. Subramanian, and M. C. R. Symons, *Chem. Commun.* **1967**, 1036, subsequently reassigned the photoproduct spectrum from ClO to ClOO.
- ¹⁰H. Okabe, *Photochemistry of Small Molecules* (Wiley, New York, 1978), p. 257.
- ¹¹C. A. McDowell, P. Raghunathan, and J. C. Tait, *J. Chem. Phys.* **59**, 5858 (1973).
- ¹²R. F. Curl, Jr., K. Abe, J. Bessinger, C. Bennett, and F. K. Tittel, *J. Mol. Spectrosc.* **48**, 72 (1973).
- ¹³P. A. McDonald and K. K. Innes, *Chem. Phys. Lett.* **59**, 562 (1978).
- ¹⁴N. Basco and S. K. Dogra, *Proc. R. Soc. London A* **323**, 29 (1971).
- ¹⁵S. Michielsen, A. J. Merer, S. A. Rice, F. A. Novak, K. F. Freed, and Y. Hamada, *J. Chem. Phys.* **74**, 3097 (1981).
- ¹⁶R. F. Curl, Jr., R. F. Heidelberg, and J. L. Kinsey, *Phys. Rev.* **125**, 1993 (1962).
- ¹⁷G. Herzberg, *Electronic Spectra of Polyatomic Molecules* (Van Nostrand, New York, 1966), p. 607.
- ¹⁸W. Craven, D. B. Knowles, J. N. Munell, M. A. Vincent, and J. D. Watts, *Chem. Phys. Lett.* **116**, 119 (1985).
- ¹⁹R. Lefebvre, *J. Chem. Phys.* **33**, 1826 (1960).
- ²⁰K. Thuomas and A. Lund, *J. Magn. Reson.* **22**, 315 (1976).
- ²¹A. Arkell and I. Schwager, *J. Am. Chem. Soc.* **89**, 5999 (1967).
- ²²H. H. Eysel and H. J. Bernstein, *J. Raman Spectrosc.* **6**, 140 (1977); M. T. Bourgeois, M. Jacon, D. Van Labeke, and H. H. Eysel, *ibid.* **6**, 146 (1977).
- ²³F. J. Adrian, E. L. Cochran, and V. A. Bowers, *J. Chem. Phys.* **56**, 6251 (1972).
- ²⁴H. S. Johnson, E. D. Morris, Jr., and J. Van den Bogaerde, *J. Am. Chem. Soc.* **91**, 7712 (1969).
- ²⁵T. Doba, K. U. Ingold, W. Siebrand, and T. A. Wildmann, *Chem. Phys. Lett.* **115**, 51 (1985), and references contained therein.
- ²⁶G. Williams, D. C. Watts, S. B. Dev, and A. M. North, *Trans. Faraday Soc.* **67**, 1323 (1971).
- ²⁷N. G. McCrum, B. E. Read, and G. Williams, *Anelastic and Dielectric Effects in Polymeric Solids* (Wiley, New York, 1976).
- ²⁸J. Wong and C. A. Angil, *Glass Structure in Spectroscopy* (Dekker, New York, 1976).
- ²⁹R. V. Chamberlin, G. Mozurkewich, and R. Orbach, *Phys. Rev. Lett.* **52**, 687 (1984).
- ³⁰W. Breinl, J. Friedrich, and D. Haarer, *Chem. Phys. Lett.* **106**, 487 (1984).