Ligand Sensitization. I. The Photo- and Oxidation–Reduction Activated Decomposition of Glacial Acetic Acid with Ceric Ammonium Nitrate[1]

T. W. Martin,[2] J. M. Burk, and A. Henshall

Contribution from the Department of Chemistry, Vanderbilt University, Nashville, Tennessee 37203. *Received September 3, 1965*

Abstract: A careful study was made of the chemical effects associated with the photon-initiated reduction of ceric ammonium nitrate in glacial acetic acid using light in the wavelength region from about 2800 to 4050 Å over the temperature range from 24 to 50°. The original cerium(IV) nitrate complex is reduced to a Ce(III) state with an experimental quantum yield (ϕ) which increases slightly from 0.36 at 30° to 0.38 at 50°. However, the true quantum yield of this reaction is always equal to ϕ_{CO_2} which increases from 0.36 at 30° to 0.46 at 50°. The major volatile decomposition products produced during steady-state irradiation were found to be carbon dioxide, nitromethane, nitric acid, and methanol, but significant amounts of methyl nitrate, methane, and methyl acetate were also obtained. Comparison of the quantum yields from flash photolysis with the steady-state results revealed the surprising fact that no nitromethane was produced using pulsed light at flash intensities. All important experimental facts, including a quantitative material balance of the products, are explained by a surprisingly simple reaction mechanism in which the major product-forming steps all proceed by the *ligand-sensitized* decomposition of acetic acid ligands activated by either an absorbed photon and/or the oxidation–reduction energy latent in the Ce(IV) to Ce(III) conversion.

Hinsvark and Stone[3] first reported using ceric ammonium nitrate, $(NH_4)_2Ce(NO_3)_6$, dissolved in glacial acetic acid as a possible strong oxidizing agent for the nonaqueous oxidation–reduction analysis of several oxygenated organic substances. These workers found this reagent system somewhat inconvenient to use because it was extremely sensitive to light as well as slightly unstable in the dark, so that it required special handling and daily restandardization for good results. Furthermore, they found that the oxidation–reduction mechanisms were usually complex and nonquantitative and sometimes involved the direct participation of the acetic acid solvent.

Preliminary studies by Martin and co-workers[4] on the possible mechanism of the photochemical instability of ceric ammonium nitrate in glacial acetic acid immediately pointed to both the unique nature and complexity of this reaction. First, carbon dioxide and methane were found to be the only volatile products readily isolated above −78°, and they were produced in the surprisingly unbalanced molar ratio of about 10 to 1. Second, the presence of methane immediately suggested that the reaction might involve intermediate methyl radicals, but attempts to corroborate this by photoinitiating the polymerization of acrylonitrile proved unsuccessful even when the yellow ceric solution was completely bleached to the colorless cerous state. Third, the reduced salt was recovered and analyzed for nitrogen to confirm that the major change upon reduction was simply the loss of one nitrate group. This loss of nitrate together with the unbalanced CO_2 to CH_4 yield showed conclusively that other decomposition products must be involved if the carbon and nitrogen material balances were to be accounted for. Thus, before any further attempt could be made to deduce a satisfactory reaction mechanism, more precise analytical methods had to be developed which would allow the complete recovery and analysis of micromolar amounts of all products from irradiated samples containing at least a 10^5-fold excess of the acetic acid solvent.

A central problem in this study from the very beginning was to explain how glacial acetic acid, which is normally such a stable molecule toward decomposition, could be so easily decarboxylated photochemically in the presence of ceric ammonium nitrate. The unusual nature of the reaction suggested that either some new reactive intermediate was formed in the primary process or else the photoexcited cerium(IV) nitrate complex was in some unique way able to transfer efficiently the absorbed energy to effect the sensitized decomposition of the solvent molecule.

The possibility that the primary process initiated by the absorbed light intensity (I_a) might lead to the production of a transient NO_3 free radical by the transfer of an electron from one of the adjacent nitrate ion ligands to the central Ce(IV) atom (reaction a) was

$$Ce^{IV}NO_3^- + h\nu \longrightarrow Ce^{III} + NO_3 \qquad (a)$$

recognized very soon after undertaking this investigation. This idea was consistent with the observed loss of one nitrate group from the Ce(IV) salt upon reduction and with the general charge-transfer character of the Ce(IV) absorption band which is quite broad and intense, having an ϵ_{max} at 3050 Å of 5890 M^{-1} cm^{-1}. We were further encouraged to believe in this intermediate NO_3 radical hypothesis upon finding methyl nitrate as a photolysis product in glacial acetic acid and by the observation of a definitive flash absorption spectrum for the NO_3 radical in 6 M aqueous nitric acid.[5] But difficulties in proving the presence of intermediate NO_3 radicals in the glacial acetic acid system

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[1] Presented in part at the 146th National Meeting of the American Chemical Society, Denver, Colo., Jan 1964, and at the Vanderbilt University Photochemistry Symposium, May 14, 1965.

[2] To whom correspondence about this paper should be sent.

[3] O. N. Hinsvark and K. G. Stone, *Anal. Chem.*, **28**, 334 (1956). The senior author is indebted to Dr. R. V. Dilts for first calling his attention to this work.

[4] T. W. Martin, J. F. Pohle, and C. Ahn, unpublished results.

[5] T. W. Martin, A. Henshall, and R. C. Gross, *J. Am. Chem. Soc.*, **85**, 113 (1963).

were soon discovered. For example, in measuring the specific rate of the back electron exchange of the NO_3 radical in 6 *M* aqueous nitric acid (reaction b) by a

$$Ce^{III} + NO_3 \xrightarrow{k_b} Ce^{IV}NO_3^- \qquad (b)$$

sensitive photomultiplier technique,[6] we attempted to detect the radical as increasing amounts of acetic acid were added to the aqueous system. The observed lifetime and strength of the radical signal progressively diminished until we were unable to find any trace of NO_3 when the added acetic acid approached 10 *M*. Whether this was evidence for a very fast reaction between NO_3 and acetic acid or evidence against the formation of the radical under these conditions was open to question, but this result precluded the possibility of finding NO_3 spectroscopically in glacial acetic acid. We were then forced to rely entirely on chemical methods hoping that good quantum yield data would prove a reliable way to deduce the correct photochemical mechanism in this solvent. How the subsequent quantum yield data succeeded in unlocking the mechanism of this complex reaction and led to a quantitative material balance on all of the products is the major purpose of this paper.

Experimental Section[7]

1. **Chemicals.** The ceric ammonium nitrate used in this study was "primary standard grade" supplied by the G. F. Smith Co. It was dried at 85° for 1.5 hr, placed in a tight screw-top bottle, and then stored in a desiccator over silica gel without further purification. Our analyses of different batches of this material indicated that its purity exceeded 99.8%.

The glacial acetic acid was Baker "analyzed" reagent grade which was subjected to further purification by the method of Eichelberger and La Mer.[8] Final recovery was carried out by fractional distillation through a 40-plate Todd column with care to exclude atmospheric moisture. The final pure material (fp 16.63 to 16.65°) was tightly stoppered and stored in a drybox. Since the freezing point of "100% pure" glacial acetic acid appears to be 16.7°,[9] our liter-scale preparations were at least 99.97% pure. Assuming water to be the most likely impurity, it is of considerable interest to our later discussion that this low impurity concentration would still be about 0.02 *M* or almost double the concentration of the ceric ammonium nitrate salt used in the samples irradiated in this study.

In order to identify and to analyze all of the volatile photochemical products, small amounts of several pure reference substances were required. Sufficient quantities of carbon dioxide were obtained *in vacuo* by cryoscopic distillation of the gas from small chunks of Dry Ice; the CO_2 was condensed at −195° after first passing through a guard trap held at −90°. The methane came directly from a cylinder (Phillips Petroleum Co.) having a stated purity of 99.50%. Milliliter quantities of the liquids (nitromethane, methanol, and methyl acetate) were purified by fractional distillation. Five-gram portions of pure methyl nitrate were synthesized by the method of Black and Babers[10] by appropriately scaling down the quantities used in their procedure. Similar amounts of pure anhydrous nitric acid were made according to the method of Taylor and co-workers.[11] Except for the nitric acid which was not analyzed further, each of these reference materials was carefully checked by gas chromatographic analysis and found free of detectable impurities.

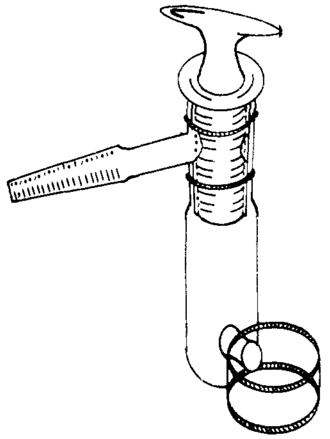

Figure 1. Pyrex photolysis cell.

2. **Sample Solutions and Cerium Salt Analyses.** Ceric ammonium nitrate is not readily soluble in glacial acetic acid, and, because there is both a very slow thermal reaction and a fast photochemical process between the Ce(IV) salt and this solvent, every effort was made to prepare sample solutions as quickly as possible, preferably at room temperature while shielding from actinic light. Solutions of approximately 0.01 *M* Ce(IV) were best prepared by placing about 5 g of the powdered dry salt into an amber glass-stoppered bottle containing 100 ml of the solvent and stirring vigorously with a magnetic stirrer for 1.5 hr. After this period, the undissolved salt was removed by rapid filtration in dim red light through two layers of medium porosity filter paper (previously dried at 110°) into a second dry amber bottle. From this filtered stock solution (which was stored in the dark no longer than 3 days) aliquots were taken for either irradiation or analysis.

Two quantitative methods were used to determine within ±0.2% the concentration of ceric ammonium nitrate in the sample solutions. In the gravimetric method, a 10-ml aliquot of stock solution was placed in a platinum crucible and warmed gently to ignite the acetic acid vapor. When only the cerium salt remained, the crucible was heated more strongly until the NO_2 fumes ceased, whereupon it was fired with a Fisher burner for 15 min before cooling and weighing as CeO_2. In the volumetric method, a 10.00-ml aliquot of the stock solution was delivered into 25.00 ml of 1.000×10^{-2} *M* ferrous ammonium sulfate in 1 *M* sulfuric acid solvent contained in a 250-ml erlenmeyer flask. Approximately 10^{-3} *M* ferroin (1 ml) was added prior to titrating the excess Fe(II) with 5.000×10^{-3} *M* ceric sulfate in 1 *M* sulfuric acid to the point where the red-amber color of the indicator just disappeared. A similar titration without any added Ce(IV) was made to obtain the indicator blank. Since the gravimetric method determines total cerium in solution rather than the specific concentration of Ce(IV), the volumetric method was considered more reliable for our Ce(III) quantum yield studies.

Early in this investigation it became of interest to determine the composition of the completely reduced cerous salt. Suitable amounts of this material were obtained by photolyzing 500-ml batches of stock solution until complete bleaching had taken place and then removing the excess solvent and volatile products at room temperature under vacuum to obtain a white salt. If the solution was heated to hasten evaporation, the distillate became yellow and the remaining salt was pale yellow in color, suggesting that partial reoxidation to Ce(IV) had occurred. On the other hand, if the salt was subjected to prolonged drying under vacuum, it was found that some NH_4NO_3 sublimed away from the original salt residue. The reduced salt was analyzed (a) for cerium by ignition to CeO_2 as described for the Ce(IV) salt, (b) for ammonium ion by the tetraphenyl boron method, and (c) for nitrate ion by precipitation as the nitron nitrate. As a means of calibrating the latter two analytical procedures, runs were made on equivalent quantities of dry ammonium nitrate salt as a reference standard.

3. **Photochemical Methods.** At the start of each photochemical experiment, 5 ml of the Ce(IV) stock solution, previously deaerated by flushing with dry helium, was pipetted into the special Pyrex photolysis cell shown in Figure 1. This cell was made by attaching a Thunberg tube to an optical cell having 2.5-cm o.d. windows, a

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[6] T. W. Martin, R. E. Rummel, and R. C. Gross, *J. Am. Chem. Soc.*, **86**, 2595 (1964).

[7] For additional details about the experimental procedures used in this work, see A. Henshall, Ph.D. Thesis, Vanderbilt University, 1963.

[8] W. E. Eichelberger and V. K. La Mer, *J. Am. Chem. Soc.*, **55**, 3633 (1933).

[9] L. F. Andrieth and J. Kleinberg, "Non-aqueous Solvents," John Wiley and Sons, Inc., New York, N.Y., 1953, p 148.

[10] A. P. Black and F. H. Babers, "Organic Synthesis," Coll. Vol. II, A. H. Blatt, Ed., John Wiley and Sons, Inc., New York, N. Y., 1943, p 412.

[11] E. G. Taylor, L. M. Lyne, and A. G. Follows, *Can. J. Chem.*, **29**, 439 (1951).

1-cm path length, and a volume slightly less than 5 ml. Its simple design was useful in degassing the sample prior to photolysis so that no residual permanent gas was detectable. This was accomplished by three consecutive freezing, pumping, and thawing cycles using a vacuum system at 10^{-5} torr. During each thawing step, the solution was agitated vigorously by rocking the cell about the side arm. After removing the sample cell from the vacuum line, it was shaken to ensure homogeneity, tilted so as to fill the optical cell, and placed together with a reference cell into an air thermostat cell compartment. This compartment was equipped to be operated either as part of a single-beam spectrophotometer for optical density measurements or as a reaction chamber for sample photolysis at constant temperature. At least 40 min was allowed for the sample to reach the desired temperature which could be controlled to ±0.1° over the range from 20 to 50°. We were limited to this small but sufficient temperature range simply because the sample froze near 16° and the acetic acid vapor dissolved the stopcock grease (Apiezon T) too rapidly to hold a vacuum above 50°.

For measuring optical densities at 4750 Å to follow the per cent of Ce(IV) reacted, in addition to the cell compartment, the optical system consisted of a steady-state light source which was a 120-v ac General Electric 100-w, base down, microscope illuminating bulb powered by a Sola constant voltage transformer; a Bausch and Lomb 500-mm model monochromator with a grating blazed for maximum transmission at about 5000 Å; a quartz lens and cell holder stop which together defined a uniformly collimated beam 19 mm in diameter through either the sample or reference cell; and a detector composed of an adjustable shutter, a 1P28 photomultiplier tube, and an Eldorado Model 201 photometer.

The potassium ferrioxalate actinometer method, fully described by Hatchard and Parker,[12] was used to measure the light intensities in the steady-state work. When exploratory experiments showed that the Ce(IV) reaction was apparently independent of wavelength in the range from about 2800 to 4050 Å (in accord with the charge-transfer character of the Ce(IV) absorption band), this entire energy range was used to irradiate the Ce(IV) sample by passing the full output of a Hanovia Type L, 450-w, quartz mercury-vapor lamp successively through a Corning 9-54 heat filter, a Corning 7-54 ultraviolet transmitting filter, and then into the Pyrex sample cell. Since each photolysis was carried out using a broad part of the mercury arc spectrum, it was necessary to determine the average quantum yield for the ferrioxalate actinometer over this range of wavelengths. This was done by weighting the individual quantum yields given by Hatchard and Parker for each of the mercury lines from 2800 to 4050 Å with regard to both their relative energy content in the spectral distribution and their relative transmissions through the two filters and the Pyrex cell windows. An average quantum yield of 1.22 over the desired range was obtained by this analysis. From this value the average light intensity used in our quantitative steady-state photolyses was computed to be $1.30 \pm 0.01 \times 10^{16}$ photons sec^{-1}. At this intensity, a typical 10-min irradiation time resulted in an 8 to 10% reduction of the initial 0.01 *M* Ce(IV) salt in a 5-ml sample and produced six volatile decomposition products which could be directly analyzed in amounts ranging individually from 0.03 to 7 μmoles. Possible complications to the product analyses because of secondary photolysis of the initial decomposition products were not serious under these conditions. There was also no interference by the slow thermal dark reaction between Ce(IV) and glacial acetic acid.

In order to check if significant changes in the quantum yields of the various primary products occurred at higher light intensity, several flash photolysis experiments were made. The same flash apparatus described elsewhere[6] was used for this work except that a Thunberg tube was attached to the side arm of the Pyrex flash cell to allow vacuum analysis of the products. It was found that five consecutive flashes taken at 1-min intervals on a single cell filling caused about the same percentage reduction of the Ce(IV) as a 10-min exposure to the steady-state arc lamp.

4. Volatile Product Separation and Analysis. After irradiation the sample was returned to the vacuum system for analysis. The first part of this problem consisted of isolating the total 8 to 10 μmoles of volatile products from nearly 5 ml of excess acetic acid solvent. This was accomplished by dynamic fractional distillation using three cryoscopic LeRoy stills[13] arranged in series with a one-stage mercury diffusion pump. In the first step of the fractionation, the entire liquid sample was distilled to the top of still 1 set at −78°, with stills 2 and 3 kept at −78 and −195°, respectively. This operation was critical in freeing the more volatile products as much as possible from the acetic acid solvent. Still 1 was specially made for this purpose so as to have about ten times more trap surface area over the same length than stills 2 and 3 which were of normal size. The frozen material at the top of still 1 was then fractionated by slowly increasing its bottom temperature from −78 to 0° over an hour period during which time all of the first product fraction (not condensable at −195°) was collected by toepling into a gas buret. Following this, the bulk of the excess solvent remaining in still 1 at 0° was isolated from the more volatile condensable products trapped in the other stills and discarded.

The noncondensable sample cut was found to contain only methane. Its yield was too small to be measured accurately with the gas buret so it was transferred by toepling *in vacuo* to a special inlet system and introduced into the gas–liquid chromatograph by which it could be analyzed with far greater precision. Two more sample cuts were separated cryoscopically. By raising the temperature of still 3 to −90°, only carbon dioxide was pumped off and its yields were large enough to be measured reliably by the gas buret. A third cut was made by raising still 2 to 0° and still 3 to −60° (the highest temperature possible to prevent acetic acid from distilling with the sample) and collecting the distillate over a 40-min period in a U-trap at −195°. The third fraction was found to contain some nitric acid, methyl nitrate, nitromethane, methanol, and methyl acetate. Although each of the products in the third fraction except nitric acid was routinely measured quantitatively by glc, their identity was first established by collecting them either prior to or after glc separation and obtaining their characteristic cracking patterns with the Vanderbilt mass spectrometer,[14] a special instrument able to handle corrosive samples such as nitric acid.

The chromatograph used in this work was a homemade instrument which featured *in vacuo* inlet systems for both condensable and noncondensable samples and a Gow-Mac Model 9193 (TE-11) thermal conductivity detector. Methane was analyzed using a 5-ft, 4-mm i.d. Pyrex glass column at room temperature packed with Linde Molecular Sieve Type 13X (previously activated for 10 min at 350° under vacuum). The third product fraction was resolved at 100° with a 9-ft, 0.25-in o.d. copper column containing 20% Carbowax 400 on Fisher Columpak (30–60 mesh). For both analyses the Gow-Mac detector was set at 130°, the filament current at 150 ma, and the helium flow rate through the sample column at 50 ml/min.

The necessary conversion factors for transforming individual glc peak areas measured by a planimeter into μmoles of a photolysis product were obtained by injecting into the chromatograph known and comparable amounts of each pure substance under identical operating conditions and measuring the resulting peak areas. The reproducibility in estimating these factors was better than ±3% for each compound.

Results and Discussion

A summary of the average experimental quantum yields (ϕ) obtained by this research, based upon an analysis for each product substance observed in both the steady-state and flash photolysis experiments, is presented in Table I. Each ϕ represents the average of at least three complete runs. The yields reported for methyl acetate, methanol, and methyl nitrate have been scaled up by 20% to correct for their approximate recovery loss during the analytical procedures. An approximate per cent standard deviation is listed to indicate the relative reliability to be attached to these data.

The markedly poorer precisions assigned to methyl acetate, methanol, and methyl nitrate deserve further comment. The lower precision for methyl acetate primarily reflects the greater difficulty in recovering this minor product reproducibly from a 10^6-fold excess of acetic acid. But the experimental yields of methanol and methyl nitrate suffer not only from fluctuations

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[12] C. G. Hatchard and C. A. Parker, *Proc. Roy. Soc.* (London), **A235**, 518 (1956).

[13] D. J. Le Roy, *Can. J. Res.*, **B28**, 492 (1950).

[14] T. W. Martin, R. E. Rummel, and C. E. Melton, *Science*, **138**, 77 (1962).

Table I. Average Experimental Quantum Yields

Temp, °C	$\phi_{Ce(III)}$	ϕ_{CO_2}	ϕ_{CH_4}	$\phi_{CH_3COOCH_3}$	ϕ_{CH_3OH}	$\phi_{CH_3NO_2}$	$\phi_{CH_3ONO_2}$	ϕ_{HONO_2}[a]
				Steady-State Photolyses				
50	0.380	0.459	0.053	0.012	0.120	0.131	0.060	0.19
40	0.376	0.430	0.050	0.008	0.152	0.122	0.025	0.23
30	0.359	0.362	0.051	0.005	0.113	0.096	0.050	0.21
				Flash Photolyses				
24	0.51	0.36[b]	0.055	0.017	0.112	Absent	0.127	0.38
±% std dev	1	4	5	20	20	5	20	c

[a] Calculated from the nitrogen material balance relation, $\phi_{HONO_2} = \phi_{Ce(III)} - (\phi_{CH_3NO_2} + \phi_{CH_3ONO_2})$. [b] Assumed value based on steady-state actinometry at 30° in order to closely reference the relative flash ϕ data with the steady-state results. [c] Not estimated since ϕ_{HONO_2} is measured indirectly.

in their recovery losses, but also because they are interconnected by a significant dark thermal hydrolysis process, $CH_3ONO_2 + H_2O \rightleftharpoons CH_3OH + HONO_2$, which has been studied elsewhere.[15] Hence, their ϕ values are strongly influenced by small changes in the degree of solvent dryness from run to run. This hydrolysis was proved to be important by fractionating unirradiated sample blanks of acetic acid spiked with both methyl nitrate and water and finding that the methanol yield increased with increasing water concentration. No such effect was found in the absence of the methyl nitrate spike. This hydrolysis is believed largely responsible for the apparent extrema observed in the trends of the steady-state ϕ values for methyl nitrate and methanol shown as a function of temperature in Table I. Presumably more impurity water was present in the 40° experiments so that ϕ_{CH_3OH} is increased by roughly the same amount that $\phi_{CH_3ONO_2}$ is decreased relative to their respective values at the other two temperatures. Thus, it is interesting to note that although the standard deviation in analyzing either methanol or methyl nitrate individually is close to 20%, the sum of both product yields shows a deviation of only about 5% because of their interconnection through this hydrolysis reaction.

It was suggested in describing our preparation of glacial acetic acid that some impurity water was probably present under the most careful conditions, approaching 0.02 *M*, which is almost double the Ce(IV) concentration used in these photolyses. Except for effecting the hydrolysis of methyl nitrate, water appears to play no part in the photochemistry of this system for we have shown that the ϕ values of the two major products, Ce(III) and CO_2, are the same within experimental error using spiked samples having a 10-fold increase in the normal water content. However, impurity water does seem to influence the structure of the photochemically reduced Ce(III) salt which is recovered upon evaporation of the volatile products and excess solvent. The analyses, presented in Table II, clearly show that this reduced nitrate salt is best characterized as the monohydrate, $(NH_4)_2Ce(NO_3)_5 \cdot H_2O$, proving that water is a far more active ligand than acetic acid in filling out the coordination vacancies in the crystallized Ce(III) nitrate salt.

Table II. Ce(III) Nitrate Salt Analyses

Salt	Analysis	% NH_4	% Ce	% NO_3
$(NH_4)_2Ce(NO_3)_5$	Theoretical	7.42	28.82	63.76
$(NH_4)_2Ce(NO_3)_5 \cdot H_2O$	Theoretical	7.15	27.79	61.48
$(NH_4)_2Ce(NO_3)_5 \cdot HOCOCH_3$	Theoretical	6.60	25.65	56.75
Recovered Ce(III) salt	Experimental	7.30 ± 0.05	27.67 ± 0.46	61.3 ± 0.1

Despite some obvious deficiencies in precision, we believe the data in Table I give sufficient insight into the photochemistry of the cerium(IV) nitrate–glacial acetic acid system to establish a detailed mechanism which explains all important features of the reaction including a complete material balance among the many products observed. This mechanism is based upon eight experimental arguments revealed by the data in Table I.

Argument 1. It is evident that ϕ_{CO_2} is either equal to or greater than $\phi_{Ce(III)}$ in the steady-state runs. This means simply that more acetic acid molecules are decomposed than Ce(IV) complexes are reduced. This fact severely limits the number of conceivable reaction mechanisms, since Ce(IV) is an efficient free-radical trap and is in large excess throughout the photolysis. For example, let us assume that the NO_3 radical is produced in the primary step similar to reaction a. If this intermediate is to lead to CO_2 it may either form secondary carboxyl or acetoxy radicals as follows.

$$NO_3 + CH_3COOH \longrightarrow CH_3ONO_2 + COOH \qquad (c)$$

$$\longrightarrow HONO_2 + CH_3CO_2 \qquad (c')$$

Once secondary radicals are formed they can be trapped by excess Ce(IV) complexes producing a second Ce(III) species, *e.g.*

$$COOH + Ce^{IV}NO_3^- \longrightarrow HONO_2 + CO_2 + Ce^{III} \qquad (d)$$

$$CH_3CO_2 + Ce^{IV}NO_3^- \longrightarrow CH_3ONO_2 + CO_2 + Ce^{III} \qquad (d')$$

Thus from either sequence, a, c, d or a, c′, d′, two Ce(III) species are produced for each CO_2, a result not in accord with the facts in Table I. Nor can the relative yields of nitric acid, methyl nitrate, and other products be explained using NO_3 as an intermediate, so step a appears to play no important role in this system.

Argument 2. The sharp drop in the $\phi_{CO_2}/\phi_{Ce(III)}$ ratio during flash photolysis and the remarkable absence of nitromethane under these conditions suggested that the steady-state route to nitromethane must also be an important source of CO_2. Additional evidence for this idea was that both $\phi_{CH_3NO_2}$ and ϕ_{CO_2} show a definite increase with increasing temperature.

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[15] J. S. McKinley-McKee and E. A. Moelwyn-Hughes, *Trans. Faraday Soc.*, 48, 247 (1952).

Argument 3. In considering the steady-state material balance for nitrogen, the sum of $\phi_{CH_3NO_2}$ and $\phi_{CH_3ONO_2}$ is far less than $\phi_{Ce(III)}$. Since the reduced Ce(III) salt analyses show clearly that only one nitrate group has been removed from the original Ce(IV) complex, $\phi_{Ce(III)}$ is then a reliable measure of the amount of nitrogen made available for product formation. Hence, it was certain that a major nitrogenous product was missing in our analyses, and we soon realized that it must be nitric acid. All attempts to devise a method for recovering and analyzing for $HONO_2$ quantitatively in this system failed. But qualitatively its presence was confirmed by the mass spectral cracking patterns of the −60° product fraction and in the glc spectrum of this fraction which always showed a prominent oxygen-like peak at about 1 min arising from its thermal decomposition. For these reasons, in devising a mechanism to fit the data in Table I, we have assumed that $\phi_{HONO_2} = \phi_{Ce(III)} - (\phi_{CH_3NO_2} + \phi_{CH_3ONO_2})$ represents a complete nitrogen balance for this system.

Argument 4. Explaining the presence of nitromethane during steady-state illumination and its complete absence at flash intensities was both the major obstacle and key in unlocking the photochemistry of this system. At first this result was taken as proof that methyl nitrate was the primary product and the probable precursor to nitromethane through a secondary reaction. This idea had to be completely rejected upon finding no nitromethane after irradiating samples spiked with methyl nitrate and/or nitric acid either by a single flash or by a series of flashes. Being then convinced that nitromethane did not come from prior photochemical products, we concluded that it must arise from some critically time-dependent phenomenon such as a diffusion-controlled reaction between two different intermediates. However, this reaction must have the constraint that at least one of the intermediates disappears so rapidly after the flash that there is not sufficient time for both to diffuse together and react to yield the nitromethane.

Argument 5. By careful correlation of all experimental results, it gradually became clear that the thermal hydrolysis of methyl nitrate could not be the only source of methanol in the steady-state experiments. It was then necessary to worry about the extent of the hydrolysis in the various quantitative runs to deduce where the additional methanol was coming from. We believe an upper limit on the extent of hydrolysis can be judged from the flash ϕ values in Table I. These data were obtained from runs made with acetic acid which was not freshly prepared and before we understood that there was a hydrolysis reaction with the methyl nitrate. They show about 47% conversion of the methyl nitrate to methanol. Upon checking this effect using the driest acetic acid we could make and the most careful technique to minimize picking up atmospheric water, we were able to make flash runs where only about 2% of the methyl nitrate was hydrolyzed. The steady-state runs at 30 and 50° were made with drier solvent and should display only a small degree of hydrolysis. For this reason, we believe the bulk of the methanol in all of the steady-state runs was produced by another process. Since the yields of methanol and nitromethane are of similar magnitude in the 30 and 50° experiments, it seemed reasonable to guess that each of these products might be formed together in the same reaction step.

Argument 6. The steady-state yield of methane is relatively minor and independent of temperature and it is essentially unchanged at flash intensities. These facts, together with the failure to find ethane as a product even at flash intensities when the conditions for radical recombination are particularly favorable because of the large extinction coefficient of Ce(IV), strongly preclude the possibility that intermediate CH_3 free radicals are the source of methane or of any other products in this system.

Argument 7. The formation of a small amount of methyl acetate when methanol is a significant photolysis product in solution with a 10^5-fold excess of glacial acetic acid did not seem unusual. So at first it was easy to presume that methyl acetate arose by a simple thermal esterification process. But it was very surprising to find that similar yields of methyl acetate were obtained on flash photolysis under conditions where only a trace of methanol was formed. Using samples of pure glacial acetic acid spiked with methanol, the esterification route to methyl acetate was proved to be unimportant. Thus the task of explaining methyl acetate as a product became of considerable interest despite its almost negligible yield.

Argument 8. Since acetic acid is the only source of carbon in this system, $\phi_{CO_2} = \phi_{CH_4} + \phi_{CH_3COOCH_3} + \phi_{CH_3OH} + \phi_{CH_3NO_2} + \phi_{CH_3ONO_2}$ should represent the carbon material balance of the photolysis products. The fact that ϕ_{CO_2} exceeds the sum of the methyl products by roughly 16% in all of the steady-state runs, even after compensating for normal recovery losses, means simply that about 16% of all methyl groups from decomposed acetic acid form a product (or products) less volatile than acetic acid and are thus not recovered to balance the CO_2 yield. Any complete reaction mechanism must be able to explain this carbon deficit in a reasonable way.

Guided by these arguments embodying the important experimental facts and constraints on this photochemical system and supplemented by other information to be described, we deduced the surprisingly complete and simple reaction mechanism set forth in Table III. It is complete in the sense that it accounts for all of the known experimental details including a quantitative material balance of the products whether they be computed collectively as total carbon and nitrogen or on an individual basis. It is simple in the sense that it reveals the complicated interplay and relative abundances of eleven products (four of which are not directly analyzable) and five postulated short-lived intermediates in only eleven steps. The specific quantum yields (Φ_i), indicating the relative contribution of each step, are calculated from the steady-state experimental ϕ values by means of the formulas in Table IV. Unequivocal confirmation of the mechanism is given by the critical tests in Table V.

Step 1 and the Nature of the Ce(IV) Complex. Step 1 is the only photon absorption process which drives the entire mechanism by producing an electronically excited (*) Ce(IV) complex. Both the absorbing and excited complexes are represented here in an abbreviated manner showing just one each of their

Table III. Proposed Reaction Mechanism

Step	Reaction	Specific quantum yields (Φ_i) 30°	40°	50°
1	$Ce^{IV}NO_3^-(HOCOCH_3) + h\nu \rightleftharpoons [Ce^{IV}NO_3^-(HOCOCH_3)]^*$	0.362	0.430	0.459
2a	$[Ce^{IV}NO_3^-(HOCOCH_3)]^* \rightarrow Ce^{III} + HONO_2 + CH_3CO_2$	0.168	0.185	0.192
2b	$\rightarrow Ce^{IV}NO_3^- + CO_2 + CH_4$	0.051	0.050	0.053
3	$[Ce^{IV}NO_3^-(HOCOCH_3)]^* + CH_3CO_2 \rightarrow Ce^{III} + 2CO_2 + CH_3OH + CH_3NO_2$	0.096	0.122	0.131
4a	$Ce^{IV}NO_3^-(HOCOCH_3) + CH_3CO_2 \rightarrow Ce^{III} + CO_2 + CH_3ONO_2 + CH_3COOH$	0.067	0.055	0.049
4b	$\rightarrow Ce^{III} + CO_2 + HONO_2 + CH_3COOCH_3$	0.005	0.008	0.012
5	$[Ce^{IV}NO_3^-(HOCOCH_3)]^* + HONO_2 \rightarrow Ce^{IV}NO_3^-(HOCOCH_3) + HONO_2^*$	0.047	0.073	0.083
6	$HONO_2^* + Ce^{III} \rightarrow Ce^{IV}\ NO_2^- + HO$	0.047	0.073	0.083
7	$HO + CH_3COOH \rightarrow H_2O + CH_2COOH$	0.047	0.073	0.083
8	$Ce^{IV}NO_3^-(HOCOCH_3) + CH_2COOH \rightarrow Ce^{III} + HONO_2 + CO_2 +$ CH_3CH_2COOH	0.047	0.073	0.083
9	$CH_3ONO_2 + H_2O \rightleftharpoons CH_3OH + HONO_2$	0.017	0.030	0.000[a]

[a] This value assumed to be zero rather than slightly negative as suggested by the analytical data in this case.

Table IV. Formulas for Calculating Specific Φ Values in Table III from Experimental ϕ Values

Step	Formulas
1	$\Phi_1 = \Phi_{2a} + \Phi_{2b} + \Phi_3 + \Phi_5 = \phi_{CO_2}$
2a	$\Phi_{2a} = \Phi_3 + \Phi_{4a} + \Phi_{4b} = \phi_{CH_3ONO_2} + \phi_{CH_3OH} + \phi_{CH_3COOCH_3}$
2b	$\Phi_{2b} = \phi_{CH_4}$
3	$\Phi_3 = \phi_{CH_3NO_2}$
4a	$\Phi_{4a} = \phi_{CH_3ONO_2} + \Phi_9 = \phi_{CH_3ONO_2} + \phi_{CH_3OH} - \phi_{CH_3NO_2}$
4b	$\Phi_{4b} = \phi_{CH_3COOCH_3}$
5	$\Phi_5 = \phi_{CO_2} - [\phi_{CH_4} + \phi_{CH_3COOCH_3} + \phi_{CH_3OH} + \phi_{CH_3NO_2} + \phi_{CH_3ONO_2}]$
6	$\Phi_6 = \Phi_5$
7	$\Phi_7 = \Phi_5$
8	$\Phi_8 = \Phi_5$
9	$\Phi_9 = \phi_{CH_3OH} - \phi_{CH_3NO_2}$

Table V. Tests of Mechanism Using Φ Values and Major Product Material Balances

Test	ϕ_{exptl} (from Table I) 30°	40°	50°	ϕ_{calcd} (from Table III) 30°	40°	50°
$\phi_{Ce(III)} = \Phi_{2a} + \Phi_3 + \Phi_{4a} + \Phi_{4b} - \Phi_6 + \Phi_8 = 2\Phi_{2a}$	=0.359	0.376	0.380	0.336	0.370	0.384
$\phi_{CO_2} = \Phi_{2b} + 2\Phi_3 + \Phi_{4a} + \Phi_{4b} + \Phi_8$	=0.362	0.430	0.459	0.362	0.430	0.459
$\phi_{HONO_2} = \Phi_{2a} + \Phi_{4b} - \Phi_6 + \Phi_8 + \Phi_9$	=0.21	0.23	0.19	0.19	0.22	0.20

coordinated nitrate ion and acetic acid ligands because this is the minimum detail necessary to describe the mechanism, since we contend that the photochemical results reported here depend upon the assumption that a nitrate ion together with at least one polarized acetic acid ligand (having its carboxyl group closely coupled to the Ce(IV) atom) are necessary to achieve the many critical transition states for energy and/or atom transfer according to this mechanism. In further support of this assumption, our solution studies of ion transference, freezing point depression, spectrophotometry, and conductivity[16] show that when ceric ammonium nitrate is dissolved in glacial acetic acid the original hexanitratocerate(IV) anion is transformed almost exclusively into a neutral tetranitrato species. Such a transformation could easily take place by a simple solvolytic displacement process, $(NH_4)_2Ce(NO_3)_6 + 2CH_3COOH \rightleftharpoons Ce(NO_3)_4(HOCOCH_3)_2 + 2\ NH_4NO_3$, in which the polarized solvent molecules have replaced two labile nitrate ions in the ligand field of the tetranitrato complex.

Step 1 is a convenient measure of the total quantum yield of this mechanism, since $\Phi_1 = \phi_{CO_2}$. Thus, the system could be used for chemical actinometry. However, since Φ_1 is less than unity, step 1 must have an appreciable back-reaction during which the absorbed photon energy is degraded as heat, and this is the meaning to be attached to the reverse arrow shown *in* step 1. The interesting temperature dependence of Φ_1 is the result of other steps in the mechanism which consume excited Ce(IV) complexes in competition with this reverse reaction.

Steps 2a, 2b, and the Meaning of Ligand Sensitization. Steps 2a and 2b are competing unimolecular decomposition paths for excited Ce(IV) complexes. Step 2a is the only source of acetoxy radical and the principal source of nitric acid and Ce(III), whereas (2b) is the only source of methane (note argument 6) in this system.

If the Ce(IV) complex were a simple molecule, then (2a) and (2b) could be described as analogous to the two classical types of unimolecular photochemical reaction, *i.e.*, homolytic and intramolecular decomposition, respectively. But coordination complexes are not simple molecules, and (2a) is obviously not a homolytic reaction but a concerted oxidation-reduction process by which the metal ion and two of its ligands are drastically changed; and (2b) is a peculiar kind of intramolecular decomposition because the product $Ce^{IV}NO_3^-$ complex can return to its original structure by simply filling out its vacant ligand shell with another polarized solvent molecule. Nor can (2b) be considered as analogous to a classical photosensitized decomposition, because the energy transfer is pictured as truly unimolecular and not bimolecular and diffusion controlled of the type $[Ce(IV)NO_3^-]^* + CH_3$-

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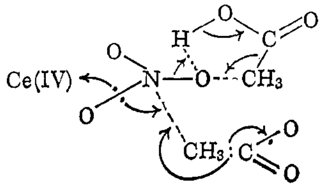
(16) T. W. Martin, A. Henshall, J. M. Burk, and R. W. Glass, unpublished work.

COOH → products. These remarks point to the need for developing new terms for discussing the interestingly different kinds of specific reactions which are unique to coordination chemistry. Toward this end we suggest the term *ligand sensitization* could be helpful in describing some reactions involving specific ligands, because the term calls direct attention to the type of reaction and its method of activation. Hence (2a) is a case of *ligand photooxidation–reduction sensitization* because both the absorbed photon energy plus the nearly 1.7 ev of energy latent in the Ce(IV) to Ce(III) couple are available to drive this reaction. Step 2b is an example of simple *ligand photosensitization* and prefixing the word ligand in this case eliminates any ambiguity as to the molecularity implied in the classical meaning of the term "photosensitization."

Step 3. This is indeed one of the most important steps in the entire mechanism and explains why nitromethane can be found after steady-state illumination but not after periodic flash photolyses (note argument 4), because the excited complex reacts or decays away too soon before the acetoxy radicals formed in (2a) can react with them. Step 3 is an example of a bimolecular photosensitized oxidation–reduction reaction but it is unusual because it involves the multiple decomposition of two different ligands as well as the attacking acetoxy radical to form only stable products. Energetically it is driven like step 2a by both photon and oxidation–reduction energies. It is the major route to CO_2 in the steady-state work and forms methanol and nitromethane in equal yields (see arguments 2 and 5). The temperature dependence noted in Φ_1 (Table III) is largely determined by this step. Because of its conceptual simplicity and since there is no evidence to the contrary, we have chosen to interpret this process as taking place by a concerted set of decompositions from a single transition state of high probability rather than by a series of consecutive steps. The structural feasibility of our point of view is demonstrated in the following crude transition-state diagram, by which it is seen that if the acetoxy radical approaches from either side of the nuclear plane of one of the NO_3^- ligands that all of the atomic nuclei required are favorably positioned so that each of the products can be formed by a concerted redistribution of the electron configuration.



Steps 4a and 4b. These steps are competitive bimolecular *ligand oxidation–reduction sensitized* processes accounting for the exclusive formation of methyl nitrate and methyl acetate, respectively. Together with step 3 they are the means of consuming all of the acetoxy radicals produced in (2a). The reason acetoxy rather than methyl radicals are used in this mechanism was given in argument 6. We conclude that the acetoxy radical is appreciably stabilized in glacial acetic acid and/or is consumed so rapidly by Ce(IV) complexes that its possible decomposition into CH_3 radical and CO_2 does not have to be considered in this system.

Steps 5, 6, 7, and 8. These four consecutuve steps are related to each other and are necessary primarily to explain the carbon-deficit problem in argument 8. They also function like step 2b in being a source of CO_2 without contributing any net change in $\phi_{Ce(III)}$, the combined effect of which allows $\phi_{CO_2} \geqslant \phi_{Ce(III)}$ as noted in argument 1.

Step 5 is a case of classical photosensitization, being a diffusion-controlled bimolecular energy transfer between an excited donor and an acceptor molecule. This process is highly probable because the ultraviolet absorption band of nitric acid nicely overlaps that of the Ce(IV) complex. In fact, OH and NO_2 radicals generated from the secondary photolysis or photosensitized decomposition of nitric acid were once considered to be the precursors of methanol and nitromethane, respectively, in this system until this route (and a comparable route using methyl nitrate) was proved untenable by the flash experiments mentioned in argument 4.

Step 6 represents to us the most unexpected reaction of the entire mechanism. It is a photosensitized oxidation–reduction process in which we postulate that a charge-stabilized $Ce^{IV}NO_2^-$ complex is formed upon releasing the OH radical. Although we can find no precedent for such an ionic complex and despite the fact that an alkali metal nitrite salt will reduce Ce(IV) in solution spontaneously, we have discovered that NO_2 gas bubbled through heated cerous nitrate in glacial acetic acid will irreversibly oxidize Ce(III) to Ce(IV), a result quite analogous to step 6. There is little question that charge-stabilized complexes are possible only in a poor ionizing solvent such as glacial acetic acid because ion-dissociation processes and certain oxidation–reduction mechanisms between the ions are inhibited. For example, it is interesting that the NO_2^- ions produced in (6) will not react with excess NH_4^+ ion to produce N_2 in this solvent.

Step 7 is a simple radical displacement process producing the carboxylmethyl radical which in turn is consumed by a *ligand oxidation–reduction sensitized* reaction (step 8) to yield propionic acid, the nonvolatile product deemed responsible for the analytical carbon deficit. It is unlikely that the combination reaction, $2CH_2COOH \rightarrow$ succinic acid, used by other workers[17] in the presence of carboxylmethyl radicals can compete with step 8 in this system.[18] Other methods of supplanting steps 5, 6, and 7 as a source of carboxylmethyl radical, such as assuming either acetoxy or carboxylmethyl radicals to be formed in step 2a or postulating the tautomerization equilibrium, $CH_3CO_2 + CH_3COOH \rightleftharpoons CH_3COOH + CH_2COOH$, gave over-all mechanisms in which the predicted material balances for Ce(III), $HONO_2$, and CO_2 did not agree with experiment.

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(17) M. S. Kharasch and M. T. Gladstone, *J. Am. Chem. Soc.*, **65**, 15 (1943).

(18) As pointed out by one referee, step 8 implies a radical displacement on tetrahedral carbon, a reaction for which there is little precedent except perhaps for the interesting example reported by D. E. Applequist, *et al.*, *J. Am. Chem. Soc.*, **82**, 2368 (1960). We believe that ligand-sensitized reactions such as presented here with the Ce(IV) system provide a unique class of reactions where concerted radical displacements on carbon may be more competitive with displacements on hydrogen. We are actively testing this hypothesis at the present time as part of the second paper in this series.

Step 9. This is the thermal hydrolysis equilibrium spoken of earlier and in argument 5. The amount of impurity H_2O in the solvent acetic acid and not the product H_2O from step 7 is the critical factor in determining the importance of this reaction.

In summary, we believe that the general photochemical mechanism by which Ce(IV) nitrate efficiently decarboxylates glacial acetic acid without utilizing intermediate NO_3 radicals is clearly established. In so doing the concept of *ligand sensitization* was defined and its usefulness demonstrated whenever a ligand actively participates in an elementary step. In the second paper of this series, we shall prove that the concept is not limited to photoinitiated oxidation–reduction reactions as seen in this study, but can be applied to interpret the unexpected chemistry of spontaneous thermal oxidation–reduction processes as well.

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Transient Electric Birefringence of Suspensions of Asymmetric Ellipsoids

Don Ridgeway

Contribution from the Department of Biophysics, Medical College of Virginia, Richmond, Virginia. *Received June 25, 1965*

Abstract: The analysis of the time dependence of the birefringence transient in the Kerr cell following sudden removal of the field is extended to include most important cases of a suspension of a monodisperse polymer representable as a rigid ellipsoid. This requires removal of two restrictions made in previous theory: the assumption of a spheroid, which excludes the ellipsoid having three unequal axes, and the condition that the applied field is everywhere normal to the axis of the Kerr cell, which neglects field end effects of importance particularly in small cells. Expressions are obtained for the birefringence of a suspension in a nonuniform field of arbitrary direction, the relaxation times for the decay in birefringence in the general case, the explicit dependence of the birefringence on the angle through which the axis of the distribution function for angular orientation of the polymer is rotated away from the normal to the cell axis in the case of the spheroid, and the correction for field nonuniformity in previous results for the case of the spheroid.

The rate of disappearance of birefringence of a solution of a polymer in the Kerr cell following sudden removal of the orienting electric field is determined by the rotational diffusion properties of the polymer. If the particular polymer can be represented in a satisfactory fashion by a model structure for which theory is available relating the optical and diffusion behavior of the model to the parameters specifying its shape, then the values of these parameters corresponding to the polymer can be estimated from birefringence data. The simplicity of the model depends on two initial decisions. First, it is necessary to determine whether the molecule behaves in orientation and diffusion as a rigid body or whether it is deformable. Second, one must specify a size range for the model, since this will determine the approximations made in the analysis of its optical and viscous properties. The present investigation is concerned with suspensions of rigid dielectric particles which are very small with respect to the wavelength of light but of sufficient size to permit introduction of macroscopic quantities, like the capacitivity, in the analysis of their polarization and rotational diffusion.

The elements of theory required to describe the variation in birefringence of a suspension following removal of an orienting field are threefold: (1) a theory of Brownian motion applicable to the shape class of the model, which introduces the rate of dissipation of energy or the time scale into the diffusion problem and which relates the macroscopic diffusion constants to the frictional constants of individual particles; (2) expressions for the frictional constants for the model, which introduce the dependence of the diffusion rate on the parameters specifying size and shape within the general shape class of the model; and (3) a theory for the birefringence of a suspension of particles of given orientation which relates the observed quantity, the retardation, to the probability density function for orientation at a given point.

The most general shape class for which all three elements of theory are available is that of the asymmetric ellipsoid. (In the following, the terms symmetric and asymmetric ellipsoid are employed to designate the spheroid of rotation and the ellipsoid possessing three unequal axes, respectively.) The theory of Brownian motion of ellipsoids has been given by Perrin,[1,2] who obtained the rotational diffusion equation for a suspension of such particles, its general

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(1) F. Perrin, *J. Phys. Radium*, [7] **5**, 497 (1934).

(2) F. Perrin, *ibid.*, [7] **7**, 1 (1936).