Mechanism of the Chromic Acid Oxidation of Secondary Alcohols. Evidence Which Establishes the Oxidative Cleavage as a One-Electron Process[1]

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Abstract: The chromic acid oxidation of 2-aryl-1-phenylethanols in aqueous acetic acid containing sodium acetate is shown to involve oxidative cleavage as well as ketone formation. Trapping experiments with oxygen show that the oxidative cleavage leads to a benzyl radical. Relative rates of ketone formation and oxidative cleavage of 2-aryl-1-phenylethanols by chromic acid in 85% aqueous acetic acid containing 0.5 *M* sodium acetate are reported. Plots of the log of these rates against σ for the substituent of the 2-aryl group show that good Hammett relationships exist with $\rho = -0.10 \pm 0.02$ for ketone formation and -1.06 ± 0.04 for cleavage. The trapping experiments and the substituent effect for cleavage indicate that the oxidative cleavage of 2-aryl-1-phenylethanols by chromic acid is a one-electron oxidation, which strongly supports chromium(IV) as the chromium species which leads to cleavage. Under these conditions, the amount of cleavage observed is *ca.* 67% and is found to be independent of the concentration of chromium(III) present. A mechanism is given which accounts for these results.

Mosher and Whitmore reported, 25 years ago, that oxidation by chromic acid in acetic acid of secondary alcohols which contain a quaternary α carbon gives products from a cleavage reaction in addition to the expected ketones.[2]

$$\text{R—CHOH—R}' \longrightarrow \text{R—CH=O} + \text{R}'\text{OH}$$

In 1956, Hampton, Leo, and Westheimer established that the cleavage brought about by chromic acid is due either to chromium(V) or chromium(IV), not to chromium(VI).[3] Since the highest amount of cleavage was found to be *ca.* 67%, these workers favored cleavage by chromium(V) as outlined by Scheme I. They also presented the mechanism shown in Scheme II which involves cleavage by chromium(IV), but did not support it, since the scheme leads to only 33% cleavage even though it accounts for all other experimental results.[4]

Scheme I

$$\text{Cr(VI)} + \text{RCHOHR}' \longrightarrow \text{Cr(IV)} + \text{ketone} \qquad (1)$$
$$\text{Cr(IV)} + \text{Cr(VI)} \longrightarrow 2\text{Cr(V)}$$
$$2\text{Cr(V)} + 2\text{RCHOHR}' \longrightarrow 2\text{Cr(III)} + 2\text{RCH=O} + 2\text{R}'\text{OH} \qquad (2)$$

Scheme II

$$\text{Cr(VI)} + \text{RCHOHR}' \longrightarrow \text{Cr(IV)} + \text{ketone}$$
$$\text{Cr(IV)} + \text{RCHOHR}' \longrightarrow \text{RCH=O} + \text{R}'\cdot + \text{Cr(III)} \qquad (3)$$
$$\text{Cr(IV)} + \text{R}'\cdot + \text{H}_2\text{O} \longrightarrow \text{Cr(V)} + \text{R}'\text{OH} + \text{H}^+$$
$$\text{Cr(V)} + \text{RCHOHR}' \longrightarrow \text{Cr(III)} + \text{ketone} \qquad (4)$$

Recently Roček and Radkowsky have shown that cyclobutanol is rapidly cleaved by chromium(IV) and is relatively unreactive toward chromium(V).[5] Moreover, we have reported that the ceric ammonium nitrate oxidative cleavage of 2-aryl-1-phenylethanols is a one-electron process.[6] Finally, Wiberg and Schäfer have shown that chromium(V) behaves like chromium(VI) and readily converts 2-propanol to acetone.[7] These recent findings[5-7] suggest that chromium(IV) is responsible for the cleavage reaction, not chromium(V). If indeed cleavage is brought about by chromium(IV), then another scheme is needed in place of Scheme II to account for the *ca.* 67% cleavage observed by Westheimer and coworkers.[3] Such a scheme, Scheme III,

Scheme III

$$\text{Cr(VI)} + \text{RCHOHR}' \longrightarrow \text{Cr(IV)} + \text{ketone}$$
$$2\text{Cr(IV)} + 2\text{RCHOHR}' \longrightarrow 2\text{Cr(III)} + 2\text{RCH=O} + 2\text{R}'\cdot \qquad (5)$$
$$2\text{Cr(VI)} + 2\text{R}'\cdot \longrightarrow 2\text{Cr(V)} + 2\text{R}'\text{OH} \qquad (6)$$
$$2\text{Cr(V)} \longrightarrow \text{Cr(VI)} + \text{Cr(IV)} \qquad (7)$$

has been presented by Roček and Radkowsky.[5] Notice that a key step in this scheme is the disproportionation of chromium(V). Also note that summation of eq 5, 6, and two times (7) gives eq 2.

The cerium(IV) oxidative cleavage of 2-aryl-1-phenylethanols was shown to be a one-electron process. This conclusion was reached because the cleaved benzyl radical could be trapped, and the ρ for the reaction was -2.0, which is closer to the range of ρ's reported for benzyl radical reactions, -0.5 to -1.5,[8] than the -4.5 to -6.5 range[9] reported for benzyl cation processes.[6] This publication reports a similar study of the oxidative

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cleavage reaction of 2-aryl-1-phenylethanols brought about by chromic acid.

Results

Oxidation of 2.4 mmol of 1,2-diphenylethanol by 1.6 mmol of chromium trioxide in 85% aqueous acetic acid gave benzyl phenyl ketone and benzaldehyde as the only products. Benzyl alcohol must be rapidly oxidized to benzaldehyde under these conditions, since, in a reaction mixture that contained 1.2 mmol of *p*-chlorobenzyl alcohol, oxidation of *p*-chlorobenzyl alcohol to *p*-chlorobenzaldehyde was so rapid that very little oxidation of 1,2-diphenylethanol took place. Thus, the oxidative cleavage of 1,2-diphenylethanol under these conditions gives two molecules of benzaldehyde. The ratio of benzaldehyde to ketone formed corresponded to *ca.* 25% cleavage. When the reaction was made 0.1 *M* in sodium acetate, *ca.* 50% cleavage occurred.

Higher concentrations of sodium acetate change the relative rates of oxidation such that benzyl alcohol can be obtained. From the chromic acid oxidation of 1,2-diphenylethanol in 85% aqueous acetic acid containing 0.5 *M* sodium acetate under a nitrogen atmosphere, 31% benzyl alcohol (based on 1,2-diphenylethanol oxidized) was obtained, which accounted for *ca.* 50% of the cleaved benzyl moiety. That the benzyl radical is a precursor of the benzyl alcohol comes from trapping experiments with oxygen. From an oxidation carried out in a comparable manner except that oxygen was bubbled through the reaction mixture, no benzyl alcohol was obtained even though a similar amount of cleavage was observed. In a control experiment, oxygen was bubbled through a heated chromium(III) solution containing benzyl alcohol, and no oxidation of the benzyl alcohol was observed. 1-*p*-Tolyl-2-phenylethanol was oxidized in 93% aqueous acetic acid containing 1 *M* sodium acetate, and the yield of benzyl alcohol was greatly diminished when the reaction was run under oxygen instead of nitrogen. In this case both benzaldehyde and *p*-tolualdehyde were produced, and the ratio of benzaldehyde to *p*-tolualdehyde increased from 0.55 for the run under nitrogen to 0.80 for the run under oxygen. These results clearly indicate that the cleavage reaction leads to a benzyl radical which can be trapped by oxygen to form benzaldehyde instead of benzyl alcohol.[10] Attempts to trap the radical by acrylonitrile or acrylamide, which was used for the cerium(IV) oxidations,[6] lead to no change in the products and no precipitate. Evidently the radical was oxidized too rapidly to be trapped by these olefins but can be trapped by oxygen.

Relative rates of ketone formation and oxidative cleavage of 2-aryl-1-phenylethanols by chromic acid in 85% aqueous acetic acid containing 0.5 *M* sodium acetate were measured by competition experiments. Equal molar amounts of two alcohols were treated with a limited amount of chromic acid and the amounts of unreacted alcohols and ketones were measured by nmr analysis. Under these conditions 55–70% cleavage of the 2-aryl-1-phenylethanols occurred.[11] Relative rates were calculated using equations derived with the reasonable assumption that the rates of chromic acid oxidation of the 2-aryl-1-phenylethanols are first order in alcohol.[12] In Table I are presented the relative rates of ketone formation and cleavage for four alcohols which were obtained from competition experiments between the *p*-methyl and parent, *p*-nitro and parent, and *p*-chloro and *p*-nitro alcohols. A *p*-chloro and parent competition was run as a check and gave k_{Cl}/k_H values of 1.03 and 0.70 for relative rates of ketone formation and oxidative cleavage, respectively. Plots of the log of these rates against σ are shown in Figure 1. These plots show that very good Hammett relationships exist with $\rho = -0.10 \pm 0.02$ for ketone formation and -1.06 ± 0.04 for cleavage. Very good correlations with σ^+ were also obtained, giving $\rho = -0.09 \pm 0.02$ for ketone formation and -0.96 ± 0.07 for cleavage, but the cleavage reaction does correlate a little better with σ than σ^+. The ρ of -0.10 for ketone formation is a good check on our method of measuring relative rates since the substituents on the 2-aryl ring are far from the hydroxyl group and thus should not affect the rates of ketone formation significantly. The ρ of -1.06 for the cleavage reaction is in the range of those observed for processes involving benzyl radicals[8] and is, in fact, even less negative than the ρ of -2.0 found for the cleavage by cerium(IV).[6]

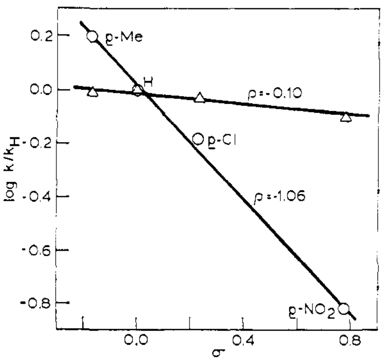

Figure 1. Plots of the logarithm of the relative rates of ketone formation (△) and cleavage (○) of 2-aryl-1-phenylethanols by chromic acid *vs.* σ of the substituent of the 2-phenyl ring.

Table I. Relative Rates of Ketone Formation and Cleavage of 2-Aryl-1-phenylethanols, $C_6H_5CHOHCH_2C_6H_4Z$[a]

Z	k_{ketone}[b]	$k_{cleavage}$[b]
p-CH_3	0.98 ± 0.02	1.57 ± 0.05
H	(1.00)	(1.00)
p-Cl	0.93 ± 0.07	0.65 ± 0.05
p-NO_2	0.80 ± 0.04	0.15 ± 0.02

[a] By chromic acid in 85% aqueous acetic acid containing 0.5 *M* sodium acetate at 85°. [b] Based on three runs.

In order to show that the amount of cleavage was independent of the concentration of chromium(III), products of a chromic acid oxidation of 1,2-diphenylethanol were measured as a function of time, and the relative per cent cleavage was found not to change as the reaction proceeded. Moreover, an oxidation was carried out in the presence of added chromium(III) and the amount of cleavage was found to be 68%, which is similar to the percentages observed in the absence of added chromium(III).

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(11) Partial oxidation of the benzyl alcohols produced from the cleavage reaction accounts for the >67% cleavage of the 2-aryl-1-phenylethanols and the variation of the amount of cleavage of these alcohols.

(12) See ref 7 and references cited therein.

Discussion

The trapping experiments and the substituent effect show that the oxidative cleavage of 2-aryl-1-phenylethanols by chromic acid is a one-electron oxidation which strongly supports chromium(IV) as the chromium species which leads to cleavage. Since *ca.* 67% cleavage was observed, Scheme III is the most reasonable mechanism for the chromic acid oxidation of 2-aryl-1-phenylethanols. Scheme I must be rejected since it involves cleavage by chromium(V), and Scheme II must be rejected since it leads to only 33% cleavage even though the cleavage step involves chromium(IV). A conceivable reaction which could lead to a large amount of cleavage by chromium(IV) would be the reaction of chromium(V) with chromium(III) to give two molecules of chromium(IV); however, no evidence that chro-

$$\mathrm{Cr(V)} + \mathrm{Cr(III)} \longrightarrow 2\mathrm{Cr(IV)}$$

mium(III) affects the amount of cleavage was obtained.

Scheme III also offers an explanation for the well documented fact that the amount of cleavage is increased by the addition of sodium acetate.[3,13] A significant decrease in overall rate of oxidation is noted when sodium acetate is added to the reaction mixture.[3] Since the rates of oxidations by chromium(VI) and chromium(V) have identical dependencies on acid,[7] both the chromium(VI) and chromium(V) oxidations of the alcohol to ketone, eq 1 and 4, must be retarded. This means that disproportionation of chromium(V), eq 7, has a greater chance to occur, and thus more cleavage by chromium(IV) should result even if the oxidative cleavage step, eq 5, is retarded to the same extent as the ketone forming steps.

Experimental Section

Methods and Materials. Equipment has been previously described.[14] Most reagents and solvents were obtained from commercial sources and purified when necessary. Chromium trioxide was obtained from Mallinckrodt and 1,2-diphenylethanol from Eastman.

1-Phenyl-2-*p*-tolylethanol. To 3.4 g (0.14 g-atom) of magnesium turnings in 300 ml of ether was added 10.6 g (0.066 mol) of α-*p*-dichlorotoluene. To the stirred Grignard reagent was added 7.0 g (0.066 mol) of benzaldehyde. After 45 min of stirring, 250 ml of 20% ammonium chloride was added to the reaction mixture, and the product was extracted with ether. The ether extract was dried ($MgSO_4$) and concentrated; the product was recrystallized from hexane to give 3.6 g (25.6%) of 1-phenyl-2-*p*-tolylethanol: mp 43–45° (lit.[15] mp 44.6–46.2°); nmr ($CDCl_3$) δ 7.26 (s, 5), 7.02 (s, 4), 4.78 (t, 1, J = 6 Hz), 2.90 (d, 2, J = 6 Hz), 2.29 (s, 3), and 2.07 (broad s, 1).

1-Phenyl-2-*p*-chlorophenylethanol was prepared from α-*p*-dichlorotoluene by the procedure used for the preparation of 1-phenyl-2-*p*-tolylethanol. The product was recrystallized twice from hexane to give 3.5 g (23%) of 1-phenyl-2-*p*-chlorophenylethanol: mp 55–56° (lit.[15] mp 55–56°); nmr ($CDCl_3$) δ 7.7–7.2 (m, 9), 4.75 (t, 1, J = 6.5 Hz), 2.82 (d, 2, J = 6.5 Hz), and 1.9 (broad, s, 1).

1-Phenyl-2-*p*-nitrophenylethanol. *p*-Nitrobenzyl phenyl ketone was prepared by the method of Corey and Schaefer[16] and recrystallized from methylene chloride–hexane: mp 143–144° (lit.[16] mp 143–144°); nmr ($CDCl_3$), δ 8.3–7.2 (m, 9), and 4.4 (s, 2). A quantity of 6.5 g of the ketone was reduced with sodium borohydride by the procedure of Berti and Marsili.[17] The reaction mixture was extracted with methylene chloride which was then concentrated, and the product was precipitated by the addition of hexane. The precipitate was recrystallized twice from methylene chloride–hexane to give 5.0 g (76%) of 1-phenyl-2-*p*-nitrophenylethanol: mp 90–91° (lit.[17] mp 91–92°); nmr ($CDCl_3$) δ 8.10 (d, 2, J = 9 Hz), 7.30 (s and d, 7, J = 9 Hz), 4.90 (t, 1, J = 6.5 Hz), 3.12 (d, 2, J = 6.5 Hz), and 2.13 (broad s, 1).

1-*p*-Tolyl-2-phenylethanol was prepared from benzyl chloride and *p*-tolualdehyde by the procedure used for the preparation of 1-phenyl-2-*p*-tolylethanol, yield 57.5%: mp 65–66° (lit.[18] mp 68–69°); nmr ($CDCl_3$) δ 7.1 (broad s, 9), 4.7 (t, 1, J = 6.5 Hz), 2.9 (d, 2, J = 6.5 Hz), 2.3 (s, 3), and 1.8 (broad s, 1).

Product Study of the Chromic Acid Oxidation of 1,2-Diphenylethanol. To 10 ml of 85% aqueous acetic acid were added 0.16 g (1.6 mmol) of chromium trioxide and 0.475 g (2.4 mmol) of 1,2-diphenylethanol. After 4 hr at room temperature 25 ml of saturated sodium chloride (satd NaCl) solution and 25 ml of ether were added to the reaction mixture. The products were extracted into the ether layer which was then washed twice with saturated NaCl solution, dried ($MgSO_4$), concentrated, dissolved in deuteriochloroform, and analyzed by nmr. Two similar oxidations were carried out, with one reaction mixture being 0.1 *M* in sodium acetate and another containing 1.2 mol of *p*-chlorobenzyl alcohol and being 0.1 *M* in sodium acetate.

Competitive Oxidations by Chromic Acid. To 7.5 ml of an 85% aqueous acetic acid solution which was 0.16 *M* in chromium trioxide and 0.5 *M* in sodium acetate was added 0.8 mmol of the two alcohols. After the solution was heated on a steam bath for 20 min and cooled, 0.565 g (0.267 mmol) of *p*-methoxybenzophenone was added. The solution was transferred to a separatory funnel and 15 ml each of saturated NaCl solution and ether were added. After extraction the organic layer was washed twice with 15-ml portions of 1 *N* sodium hydroxide and dried ($MgSO_4$). The ether was distilled and the residue was dissolved in deuteriochloroform and analyzed by nmr.

Relative extraction ratios were determined as follows. Known amounts of the alcohols, the corresponding ketones, and the standard were added to an artificial reaction mixture that had been prepared by reducing an 85% aqueous acetic acid solution, which was 0.16 *M* in chromium trioxide and 0.5 *M* in sodium acetate, with 1.4 mmol of pinacol. This solution was then worked up and analyzed in the same manner as the reaction mixtures. These extraction ratios ranged from 0.956 to 1.06.

The amounts of alcohols and ketones were determined by integration of the nmr peaks for the methylenes of the alcohols ($\delta \sim 3.0$ d), the methylenes of the ketones ($\delta \sim 4.2$ s), and the methyl of the standard (δ 3.8 s). In most cases a sweep width of 500 Hz and the average of three integration sweeps per spectrum were used. In the runs involving the *p*-nitro alcohol the downfield peak of the *p*-nitro alcohol and the upfield peak of the other alcohol were separate, but the other two peaks were superimposed. It was determined that for the three alcohols involved in these runs the ratio of the upfield to downfield peaks was (45.0 ± 0.3)/(55.0 ± 0.3). Thus the amount of each alcohol was determined by measuring one peak and multiplying by the approprirate factor to account for the other peak. In the cases of the *p*-methyl alcohol *vs.* the parent and the *p*-chloro alcohol *vs.* the parent the separations of the peaks for both the alcohols and ketones were small. Thus the peaks were expanded with a sweep width of 50 Hz (with the rf field lowered to a point below saturation) and the areas of the peaks were measured by planimetry. In these runs all four alcohol peaks could be measured since the doublets overlapped, with one peak of each doublet between the two peaks of the other doublet.

Relative rates of ketone formation are given by eq 8, and relative rates of oxidative cleavage are given by eq 9, where X_0

$$(k_x/k_y)_{\mathrm{ketone}} = \left(\frac{\log (X_0/X_f)}{\log (Y_0/Y_f)}\right)\left(\frac{\mathrm{Ket}_x/(X_0 - X_f)}{\mathrm{Ket}_y/(Y_0 - Y_f)}\right) \quad (8)$$

$$(k_x/k_y)_{\mathrm{cleavage}} = \left(\frac{\log (X_0/X_f)}{\log (Y_0/Y_f)}\right) \times \left(\frac{(X_0 - X_f - \mathrm{Ket}_x)/(X_0 - X_f)}{(Y_0 - Y_f - \mathrm{Ket}_y)/(Y_0 - Y_f)}\right) \quad (9)$$

and X_f are initial and final concentrations of alcohol X, Y_0 and Y_f are initial and final concentrations of alcohol Y, and Ket_x and Ket_y are final concentrations of the ketones produced from alcohols X and Y, respectively.

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Chromic Acid Oxidation of 1-*p*-Tolyl-2-phenylethanol in the Presence of Acrylamide or Acrylonitrile. To 50 ml of the normal reaction mixture was added 5 g of acrylamide or acrylonitrile. After the oxidation, the reaction mixture was worked up and analyzed by nmr as described for the competition studies.

Radical Trapping Experiments with Oxygen. A chromic acid oxidation of 1,2-diphenylethanol was carried out in the normal fashion except that oxygen was bubbled through the reaction mixture during the oxidation. In a control experiment, nitrogen was bubbled through the solution instead of oxygen. In another experiment, benzyl alcohol was added to a prereduced chromium solution, and oxygen was bubbled through the solution while it was heated for the same amount of time needed to oxidize the 1,2-diphenylethanol. All of these runs were worked up and analyzed as described for the competition runs.

1-*p*-Tolyl-2-phenylethanol was oxidized by chromic acid in 93% acetic acid being 1 *M* in sodium acetate, with oxygen bubbling through the reaction mixture in one run and nitrogen bubbling through the reaction mixture in another run. These runs were worked up and analyzed as described for the competition runs except that no standard was added.

Products of the Chromic Acid Oxidation of 1,2-Diphenylethanol as a Function of Time. To 12.5 ml of 85% acetic acid, 0.5 *M* in sodium acetate, was added 4 mmol of 1,2-diphenylethanol. In another flask 4 mmol of chromium trioxide was dissolved in 12.5 ml of the solvent. Both solutions were heated to 77°, flushed with nitrogen, combined, and kept at 77° under nitrogen. Aliquots of 5 ml were taken after 1, 5, and 10 min and were added to 10 ml of a cooled saturated NaCl solution. The standard was added with 10 ml of ether and the mixtures were worked up and analyzed as described for the competition runs.

Products of the Chromic Acid Oxidation of 1,2-Diphenylethanol in the Presence of Added Chromium(III). 1,2-Diphenylethanol (1.6 mmol) was dissolved in 7.5 ml of the prereduced chromium solution and 1.2 mmol of chromium trioxide was added. After the reaction mixture was heated for 20 min, 7.5 ml of 85% acetic acid, 0.5 *M* in sodium acetate, was added along with 0.565 g of the standard, and the mixture was worked up and analyzed as described for the competition runs. In the control experiment, the alcohol and chromium trioxide were dissolved in 7.5 ml of 85% acetic acid, 0.5 *M* in sodium acetate. After heating, 7.5 ml of the prereduced chromium solution and 0.565 g of the standard were added and the mixture was worked up and analyzed.

Positive and Negative Ion–Molecule Reactions and the Proton Affinity of Ethyl Nitrate

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Abstract: Ion cyclotron single and double resonance techniques have been used to study the positive and negative ion–molecule chemistry of ethyl nitrate. The positive ion–molecule reactions can be divided into three classes: (1) transfer of NO_2^+ from $CH_2ONO_2^+$ and $H_2NO_3^+$ to ethyl nitrate to form $C_2H_5N_2O_5^+$; (2) protonation of ethyl nitrate by $C_2H_3^+$, $C_2H_5^+$, and CHO^+; and (3) fragmentation of protonated ethyl nitrate into $H_2NO_3^+$ and ethylene. Proton transfer reactions were used to determine that $\Delta H_f(C_2H_5ONO_2H^+) = 149 \pm 3$ kcal/mol, corresponding to a value of 180 ± 3 kcal/mol for the proton affinity of ethyl nitrate. The only negative ion–molecule reactions in pure ethyl nitrate are the reactions of $C_2H_3O^-$, $C_2H_5O^-$, and OH^- to produce NO_3^-. Mixtures of ethyl nitrate with methanol, ethanol, 2-propanol, acetone, propionaldehyde, and *n*-propyl chloride showed that most of the negative ion reactions were proton transfers, although several displacement-like reactions were also found. The NO_2^- ion was completely unreactive. A value of $\Delta H_f(CH_3O^-) = -30 \pm 6$ kcal/mol is deduced from the observed proton transfer reactions. The large cross section at zero electron energy for the formation of NO_2^- by dissociative resonance capture makes ethyl nitrate an excellent detector for near-zero energy electrons. An electron impact excitation spectrum of carbon disulfide was obtained using the NO_2^- peak from ethyl nitrate to monitor the number of inelastically scattered electrons as a function of electron energy.

Although the positive[2,3] and negative[4] ion mass spectra of ethyl nitrate have been studied in some detail, no study of the gas phase ion–molecule chemistry of this or any other nitrate has been reported. In view of the richness of the ion–molecule chemistry of the nitroalkanes,[5] ion cyclotron resonance (ICR) spectrometry has been used to study the positive and negative ion–molecule reactions in ethyl nitrate.

An ICR spectrometer[6,7] is capable of operating at pressures and ion residence times such that extensive ion–molecule reactions can occur. Ion detection and mass resolution are based on the fact that an ion of mass m in a uniform magnetic field H moves in a circular orbit with angular frequency

$$\omega_c = qH/mc$$

where q is the ion charge and c is the speed of light. If an rf electric field $E_1(t)$ is applied perpendicular to H at the cyclotron frequency ω_c of one of the ionic species present, then those ions will absorb energy from the electric field and be accelerated to larger cyclotron orbits and kinetic energies. Sweeping the magnetic field while recording the power absorbed from a fixed-frequency marginal oscillator detector produces a mass spectrum of the ions in the spectrometer. In addition to this single resonance experiment, a double resonance technique is also available which

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