

Ozonation of Phenol in Water Studied by Electron Tunneling^{1a}

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Publication costs assisted by Ecole Polytechnique and Yale University

We have obtained the tunneling spectra of 100 ppm phenol solution before and after ozonation. The spectra are in excellent agreement with those of concentrated phenol and acetic acid, respectively, indicating that inelastic electron tunneling spectroscopy can be used to detect the presence of phenol in water at concentrations of probably 10 ppm or less. We have also obtained and compared the spectrum of partially ozonated phenol with two previously proposed mechanisms for phenol ozonation. The intermediates present in the spectrum could be those predicted by Bailey's but not by Eisenhauer's ozonation mechanisms.

1. Introduction

We have previously shown that it is possible to use inelastic electron tunneling spectroscopy, IETS, in the detection of organic compounds present at very low concentrations in water.² Detection of impurities is accomplished by the identification of bond types from vibrational frequencies which correspond to peaks in the tunneling spectra, and of molecular species from the voltage (group frequencies) at which these peaks occur. If proper care is exercised, we find that the intensity of these peaks will be related to the concentration of the molecule in solution. Work done on similar junctions doped with pure organic compounds³ has shown that IETS has sufficient sensitivity to differentiate many of the characteristic modes of straight chain hydrocarbons, amino acids, aromatic ring compounds, pyrimidine bases, cyclic saturated hydrocarbons, and other nonaromatic ring compounds. Normally it should be possible for the same differentiation to be made in the case of aqueous solutions of the above compounds. In this paper, we apply the same method to a study of the ozonation of water solutions of phenol.

Phenol is contained in many industrial wastes, and frequently as an impurity, in drinking water. When present, even in trace amounts, too low to be chemically detected, it gives water an objectionable taste and odor.^{4,5} The most efficient method of phenol removal is ozonation. The mechanism as well as the technology of ozonation have been described by Ryan.⁶ During ozonation, the phenol solution assumes a deep amber color, which starts disappearing after about one-third of the phenol has been oxidized. After all the phenol has oxidized, the solution again becomes colorless. This color is attributed to the formation of intermediate compounds of unknown composition in the solution.

The objectives of our experiments were to apply IETS in the detection of phenol in the ppm range, to detect its disappearance, and to obtain a spectrum of the intermediate compounds that are responsible for the yellow color of the solution, in order to attempt to identify them.

Tunnel junctions were prepared, as described earlier,² by dipping an aluminum electrode in the appropriate water solution, allowing the sample to dry, and evaporating a lead counterelectrode. In addition to hand-dipping the Al strip,

in air, as described in our earlier paper,² we have also prepared junctions by introducing clean dry oxygen and the appropriate solutions directly into the evaporation vacuum system and moving the solution into contact with the Al film.⁷ The latter method gives quantitatively more reproducible results than the former, but the two approaches yield the same results in all other respects.

Experimental curves of d^2I/dV^2 vs. V were obtained by methods which are now well known.²

II. Identification of Phenol in Water

Figures 1 and 2 show inelastic tunneling spectra for 1% and 100 ppm phenol in water, respectively. The peak locations in these spectra are listed in Table I. They are in excellent agreement with those obtained by vapor doping by Lewis et al.,⁸ as well as with the results of ir studies by Taylor and Ludlum.⁹ The figures show an overall increase in peak intensities with increasing concentration, compared to the 450-meV (3627 cm^{-1}) peak which is due to water. In addition, there is an increase in the intensities of the 352-, 360-, and 378-meV (2838 , 2902 , and 3047 cm^{-1}) peaks relative to the 367-meV (2958 cm^{-1}) peak as well as an increase in the 133- and 144-meV (1073 and 1162 cm^{-1}) peaks relative to the 139-meV (1121 cm^{-1}) peak.

These two groups of peaks correspond to the C-H stretch and bending modes, respectively. Since neither the 367- nor the 139-meV peaks appear in Lewis's⁸ spectrum it may be concluded that they are both due to impurities present in the system, and that they are suppressed as the phenol concentration increases. Although the sensitivity limit of the IETS method was not tested, the peak intensities for the 100 ppm solution are strong enough to suggest that 10 ppm can easily be detected and that it may be possible to detect another order of magnitude lower concentration.

When a 100 ppm phenol solution was ozonated for 5 min under the conditions described in the next section, the characteristic odor of phenol disappeared without the solution having changed color at any time during the ozonation process. The spectrum of the ozonated solution is shown in Figure 3. Here no traces of phenol are left; the spectrum resembles that of acetic acid, which is known to be one of the products of phenol ozonation.⁶ Its spectrum is also shown

TABLE I: Peak Positions of C₆H₅OH Adsorbed on Al₂O₃^a

1% C ₆ H ₅ OH			100 ppm C ₆ H ₅ OH			Comments
meV		cm ⁻¹	meV		cm ⁻¹	
43.5	w	351	44	w	355	x sensitive
49.5	s	399	48.5	s	391	Ring deformation
58	m	468	56	m	452	
71	w	573	71	m	573	
77	m	621	76.5	m	617	Ring deformation
87	s	702	86.5	s	698	Ring deformation
91	s	734	91	s	734	C-H bend?
99	w	799	99	m	799	x sensitive?
104	s	839	104.5	s	834	O-H bend, Al-O stretch
114	s	920	113.5	s	916	O-H bend, Al-O stretch
121	s	976	120.5	m	972	O-H bend, Al-O stretch
128	w	1033	128	w	1033	C-H bend
133	m	1073	131	w	1057	C-H bend
139	m	1121	138	m	1113	C-H bend
144	m	1162	144	w	1162	C-H bend
			148	w	1194	
158	s	1275	156	s	1258	x sensitive, C-O stretch
			162	w	1307	Ring stretch with O-H bending character
171	m-s	1379	170.5	s	1375	Ring stretch with O-H bending character
179.5	s	1448	178.5	s	1440	Ring stretch
198	s	1597	198	s	1597	Ring stretch
209.5	m	1690	210	m	1694	Ring stretch
			226	b	1823	2 × 113.5
352	sh	2838				
360	s	2902	360	s	2902	C-H stretch
367	sh	2958	367	s	2958	C-H stretch
378	s	3047	378	sh	3047	C-H stretch
417	?	3364				O-H stretch
450 ± 2	s	3627 ± 16	450 ± 2	s	3627 ± 16	O-H stretch

^a In this and subsequent tables, unless otherwise indicated, the uncertainty in peak position is on the order of ±1 meV (±8 cm⁻¹). b = broad; m = medium; s = strong; sh = shoulder; w = weak; x = substituent on the aromatic ring.

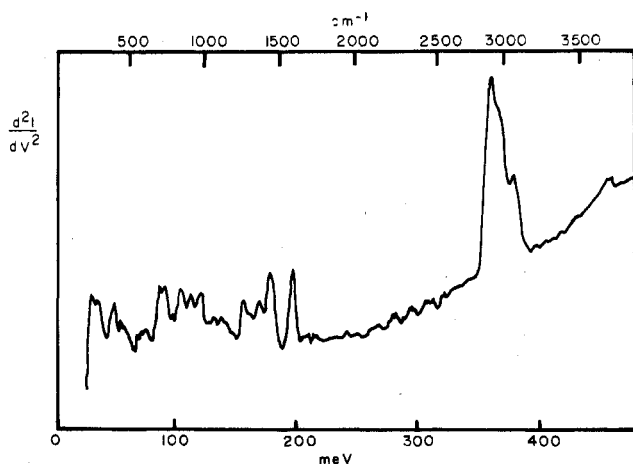


Figure 1. Electron tunneling spectrum of junction exposed to 1% C₆H₅OH solution.

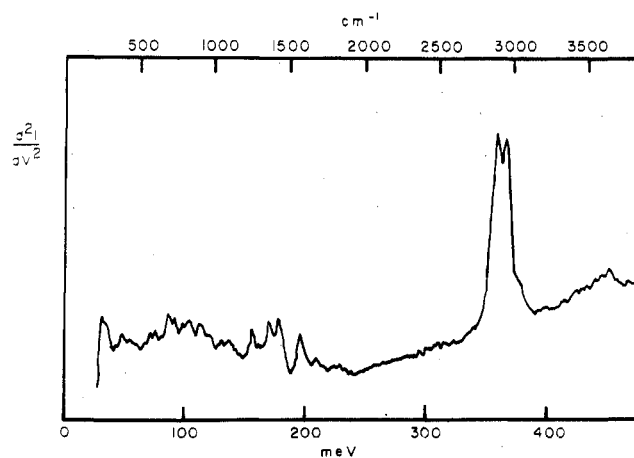


Figure 2. Electron tunneling spectrum of junction exposed to 100 ppm C₆H₅OH solution.

in Figure 3. Thus, in the present case, virtually all the phenol has been oxidized, and the intermediate compounds did not produce any detectable coloration of the solution, apparently due to their very low concentration.

III. Intermediate Compounds

Experiment and Results. In an attempt to obtain the spectrum of the intermediate reaction compounds which are produced during the oxidation of phenol, and are re-

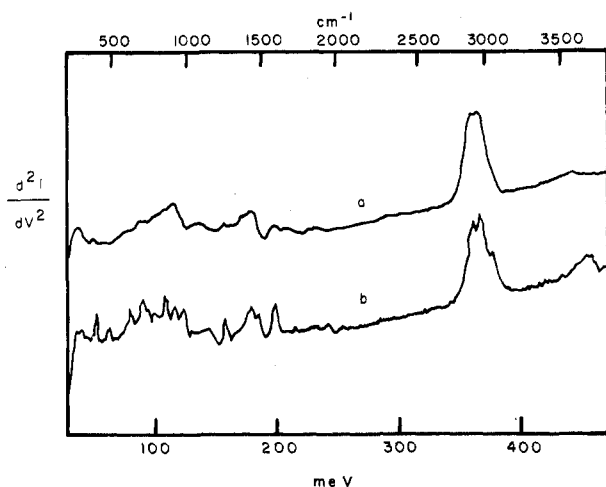


Figure 3. Electron tunneling spectrum of 100 ppm solution ozonated for 5 min showing the disappearance of phenol (a) compared with CH_3COOH spectrum (b).

sponsible for the yellow color of the solution, a 1% phenol solution was ozonated for 1 hr using a Welsbach laboratory ozonator, Model T-408, operating at 70 V with an input O_2 pressure of 8 psi and a flow of 1 l./min. With solutions of this concentration, the yellow color appears after a few minutes and gets continuously deeper as ozonation continues. After 1 hr, the solution has a deep yellow-amber color.

Repeated attempts to dope the junctions with ozonated solution failed, as the junction had impedances greater than 100 k Ω and were therefore unfit for d^2I/dV^2 measurements. Junction impedances continued to be high in spite of short oxidation times, even though the same solution would produce low impedance junctions when not ozonated. In order to reduce the oxidizing effect of the solution it was diluted to one part of solution in four parts distilled water, and then to one part of solution in 19 parts water. The 1:4 solution produced junctions of over 20-k Ω impedance, while samples doped with 1:19 solution had impedances of 5 k Ω and greater. In all cases, the samples had low impedances at first, but they were extremely noisy and tended to increase in impedance as a bias of a few hundred millivolts was applied. After a few hours with the bias on at room temperature the impedances tended to be too big for measurements, while the noise was practically gone. Evidently, oxidation of the aluminum caused by the presence of the compounds in the solution continues taking place for hours after a bias is applied to the sample. This is to be expected in view of the relatively unstable character of the intermediate solutions, many of which probably involve zwitterions having $\text{HC}^+-\text{O}-\text{O}^-$ groups according to the ozonation mechanism proposed by Bailey et al.¹⁰ Normally the negative end of the molecule should go to the Al sites and oxidize them further.

The tunneling spectrum of a junction doped with a partially oxidized phenol solution is shown in Figure 4. Table II lists the peak energies for this spectrum. The presence of phenol in this case is easily confirmed from the characteristic peaks at 49.5, 172, 179.5, and 199 meV (399, 1387, 1448, and 1605 cm^{-1}), corresponding to the ring stretching and deformation modes and the C-H bend and stretching modes marked in the table.

Due to the reduced sensitivity in obtaining the ozonated phenol spectrum (since the corresponding samples could

TABLE II: Peak Positions of 1% $\text{C}_6\text{H}_5\text{OH}$ Ozonated for 1 hr and Adsorbed on Al_2O_3^a

meV		cm^{-1}	Comments
49.5	s	399	Ring deformation
59.5	s	480	
79	w	637	
90	s	726	C-H bend ?
108	s	871	
114	s	920	O-H bend, Al-O stretch
117	s	944	O-H bend, Al-O stretch
122	s	984	O-H bend, Al-O stretch
135	m	1089	C-H bend
143	m	1153	C-H bend
158	s	1274	x sensitive
172	sh	1387	Ring stretch with O-H bending character
179.5	s	1448	Ring stretch
199	s	1605	Ring stretch
210	w	1694	Ring stretch
214	m	1726	
356	?	2870	C-H stretch
360	s	2902	C-H stretch
367	sh	2956	C-H stretch
378	s	3047	C-H stretch
395	m	3184	
450	s	3627	O-H stretch

^a One part of the ozonated solution was diluted with 19 parts of distilled water before introducing it to the sample. b = broad; m = medium; s = strong; sh = shoulder; w = weak; x = substitute on the aromatic ring.

not be produced with optimum impedances) certain weak phenol peaks are missing from the spectrum of Figure 4. Those should have been at 43.5, 71, 99, 128, and 417 meV. However, in addition to the phenol peaks, there is new structure at 108, 117, 214, and 395 meV; and the peaks at 77, 133, and 352 meV have shifted to 79, 135, and 356 meV, respectively, indicating bonds of basically the same type, but in slightly different environments which alter the force constants and/or the reduced masses of the bonded groups. Another difference to be noted is the change in the relative intensities of some peaks. Thus, the 172-meV peak of Figure 4 is much less intense than the corresponding peak at 171 of Figure 2 when they are both compared against the 179.5-meV peaks.

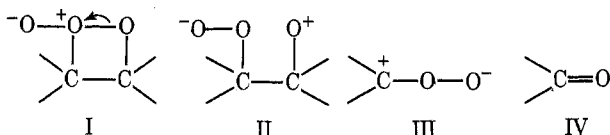
Interpretation of the Spectrum. For an interpretation of the spectrum of the partially ozonated phenol given in Figure 4 and in Table II, two existing theories were considered, and an attempt was made to assign the absorption peaks of the spectrum to excitations of the intermediates predicted by those theories. A satisfactory assignment could only be made for the intermediates proposed by Bailey et al.¹⁰ described below, while Eisenhauer's¹¹ proposed intermediates could not possibly be present in our spectrum. The chief argument against some of Bailey's structures being present as intermediate compounds in the solution is their relative instability. The spectrum of Figure 4 was obtained from a junction doped with a solution that had been ozonated over 1 month before it was employed. The solution still had the characteristic yellow color of partially oxidized phenol; normally some of the intermediates discussed below would be expected to react and form more stable compounds in that interval. However, as will be shown below, one of the compounds which should be

formed according to the Bailey et al. model¹⁰ would be stable and detectable.

Bailey et al.'s theory¹⁰ of ozonation of an aromatic nucleus assumes that an initial electrophilic attack on the ring by one of the terminal oxygen atoms of the ozone molecule is followed by a nucleophilic attack by either the other terminal atom or the central atom to produce the following structures respectively:

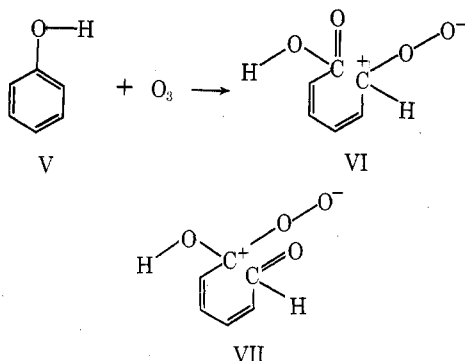


Of the above structures the second has never been isolated in any compound although theoretically it is stable and it should have been observed if it existed. The first structure, I, should be unstable, with the O-O bond breaking to produce structure II, which in turn would decompose into structures III and IV since the positive charge on the oxy-

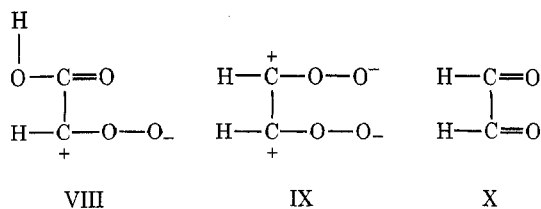


gen would attract the electrons of the C-C bond and weaken it. This theory has proven to be consistent with experimental results including the ozonation of the *o*-xylene, as described by Ryan.⁶ Following the mechanism of ozonation of *o*-xylene described by Ryan, it is possible to construct a similar mechanism for the ozonation of phenol.

An electrophilic attack on phenol would produce the following two zwitterions:



These would be further ozonated into



The products from VIII and IX would be

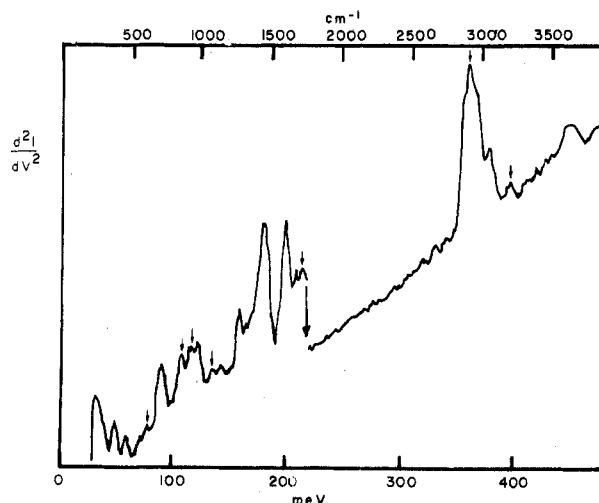
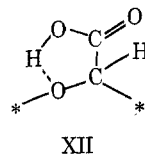
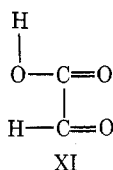


Figure 4. Electron tunneling spectrum of partially oxidized 1% C_6H_5OH solution showing the characteristic phenol peaks as well as new structure. The peaks referred to in Table III are indicated by small arrows. The long arrow indicates a shift of the zero.

and X, respectively. The spectrum of Figure 4 can be analyzed with the above intermediates in mind.

The peak at 214 meV (1726 cm^{-1}) must almost certainly be due to a C=O bond since virtually all of the attributable peaks at this energy have been attributed to C=O.¹² Low-energy peaks of skeletal vibrations are not usually reliable in bond identification because their energies tend to change drastically with changes in the immediate environment of the vibrating group; however, they may be taken as an indication that a particular bond exists. In the present case a comparison of Tables I and II shows that a new peak at 108 meV (871 cm^{-1}) has emerged in the spectrum of the intermediate compounds. This may be due to an O-O vibration which is at 877 cm^{-1} (109 meV) in H_2O_2 ¹³ and varies between 833 and 952 cm^{-1} (103 and 118 meV) in peroxides, hyperoxides, and peracids.^{14,15} However, structures VIII and IX, above having O-O bonds, are highly unstable and thus unlikely to be present in our solution. On the other hand, the ir spectrum of structure XI, glyoxylic acid, when in the vapor state, shows a peak due to an in plane vibration at 866 cm^{-1} (107.5 meV),¹⁶ and the 108-meV peak could be attributed to this mode more suitably.

Bonds with vibrational energies of 395 meV (3184 cm^{-1}) are usually those involving nitrogen and hydrogen, such as NH, NH_2 , NH_3 , and NH_4 in various configurations. Assuming no appreciable contamination in the system, all of the above may be ruled out. The only remaining alternative is a downshifted O-H bond as a result of intramolecular hydrogen bonding. A strong intramolecular hydrogen bond can shift the OH frequency as low as 310 meV although such strong hydrogen bonds usually give rise to broad bands.¹⁷ Intramolecular hydrogen bonding to the alumina surface can be ruled out because this would produce a broad band extending all the way up to 450 meV due to surface heterogeneity. Species XII which may be considered the product

TABLE III: Ir Spectrum of Glyoxylic Acid in Vapor State^a and IETS Peaks Not Attributed to Phenol in the Partially Ozonated Phenol Spectrum

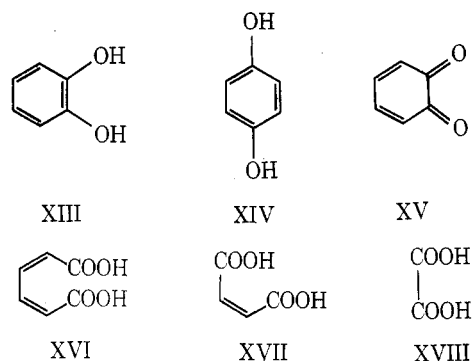
Ir		IETS		Ir		IETS	
meV	cm ⁻¹	meV	cm ⁻¹	meV	cm ⁻¹	meV	cm ⁻¹
435	3510			150	1205		
		395	3184				
356	2867					135	1089
355	2860	356	2870	123	992		
354	2851			122	982		
225	1817			119	960		
224	1809			117	948	117	944
223	1799			116	935		
219	1764			109.5	884		
218	1755	214	1726	108.5	876	108	871
216.5	1746			107.5	866		
172	1390			96	773		
171	1382			82	660		
168	1358			80	645	79	637
167	1348						
166	1341						
164	1320						
162	1305						

^a Reference 16.

of associative adsorption of glyoxylic acid, XI, is consistent with the major features of the observed spectrum. The peaks at 395, 356, and 214 meV (3184, 2870 and 1726 cm⁻¹) are assigned to the intramolecular hydrogen bonded OH, C-H, and carbonyl, respectively. Normally acids adsorb on alumina surfaces by dissociative adsorption of the carboxylic group.¹⁸ We discount this structure in the present study since the antisymmetrical and symmetrical frequencies of the carboxylate group that occur between 1610–1550 and 1400–1300 cm⁻¹ (200–190 and 175–160 meV), although not absent, are probably due to phenol (see Table I) and this structure would not explain the absorbance at 395 meV. It would be easy to understand how the surface species XII could be formed from the intermediate VII, but the actual precursor which apparently exists in the ozonated phenol solution is of unknown structure. The surface species analogous to XII that could be formed from X should give rise to two C-H bands and is, therefore, probably not present on the surface. Table III lists the ir spectrum of glyoxylic acid together with all new and shifted peaks that appear in the spectrum of partially ozonated phenol in Table II. Except for the large shift to lower frequency of the OH (attributed to intramolecular hydrogen bonding) and a small shift to higher frequency for the carbonyl, the tunneling spectrum of the surface species has much in common with the ir spectrum of glyoxylic acid in the vapor state. The intramolecular hydrogen bonding postulated for the surface species is unlikely in the gas phase because the sp² hybridization of the carbon (compared to sp³ of XII) would make the geometry unfavorable. Confirmation of structure XII could be obtained by deuteration to determine that the 395 meV peak is, in fact, due to hydrogen.

Another ozonation mechanism was proposed by Eisenhauer.¹¹ According to this mechanism the first step in the oxidation of phenol is the formation of catechol (XIII) and hydroquinone (XIV). The next step involves the formation

of *o*- and *p*-quinone from catechol and hydroquinone, respectively. Subsequently the quinone ring (XV) is broken and muconic acid (XVI) is formed. This in turn is oxidized into maleic (or fumaric) (XVII) and finally into oxalic (XVIII) acid.



All of the above intermediates, with the exception of hydroquinone, would be expected to be stable; and quinone might be responsible for the yellow coloring of the solution. However, at no point during oxidation did the solution assume a pink or green color characteristic of hydroquinone and catechol as reported by Eisenhauer.¹¹ Furthermore, the visible light absorption spectrum of the intermediate compound solution did not match the corresponding spectrum of quinone. In particular, the shoulder between 420 and 460 nm in the absorption spectrum of quinone was missing.

The absence of quinone and catechol from the spectrum is concluded from the absence of the 202-, 195-, 192-, 162-, 149-, 129-, 109-, and 78-meV peaks for catechol and the 353-, 194-, 191-, 181-, 174-, and 48-meV peaks for quinone.¹⁷ In particular, the absence of a 1670-cm⁻¹ (207 meV) carbonyl frequency is a strong indication to that effect.

The absence of C=C peaks for the nonaromatic molecules at 1600–1680 cm⁻¹ (~ 199–208 meV) eliminates the possibility of muconic acid in the solution; however, fumaric (or maleic) acid may still be present and not absorb in this band because of the symmetry of the molecule about the C=C bond. Unfortunately, the symmetric and asymmetric COO modes that should appear if the acids were present cannot be distinguished from the 179.5- and 199-meV peaks of phenol in the spectrum.

Finally, the spectrum of Figure 4 does not agree with the spectra of fumaric and maleic acids, whose peak locations are given in Table IV.

IV. Conclusion

We have obtained the tunneling spectra of 100 ppm phenol solution before and after ozonation. The spectra are in excellent agreement with those of concentrated phenol and acetic acid indicating that IETS can probably be used to detect the presence of phenol in water at concentrations of 10 ppm or less. We have also obtained the tunneling spectrum of partially ozonated phenol, containing intermediate reaction complexes, as shown by the deep yellow color of the solution. This spectrum has been compared with two previously proposed mechanisms. In the case of Bailey's model¹⁰ the intermediates were obtained by proceeding in a manner analogous to that of Ryan⁶ for *o*-xylene. The intermediates to be expected on the basis of Eisenhauer's model¹¹ were worked out by Eisenhauer himself. Our results seem to agree with Bailey's mechanism rather than

TABLE IV: Ir Spectra of Fumaric and Maleic Acids^a

Fumaric acid		Maleic acid	
meV	cm ⁻¹	meV	cm ⁻¹
123	992	108	870
124	1000	109	880
149	1205	151	1220
153	1235	155	1250
159	1282	177	1430
170	1370	181	1460
175	1408	190	1530
180	1449	197	1590
207	1667	203	1640
326	2632	212	1710
365	2941	322	2600
		359	2900

^a From ref 19.

Eisenhauer's even though this requires that a large portion of glyoxylic acid adsorb on alumina without breaking of the O-H bond as is normally observed with organic acids. Further experiments on ozonation particularly using deuterated phenol could clarify this matter.

Kinetics of Spur Reactions of Electrons in Ethylene Glycol-Water Glassy Ice. A Pulse Radiolytic Study

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Revised Manuscript Received September 12, 1975)

Ethylene glycol-water glasses were pulse irradiated at 173 K. It has been found that Cd²⁺ ions react with both trapped electrons (e_t^- , $k = (2.5 \pm 1) \times 10^5 M^{-1} \text{sec}^{-1}$) and with their precursors ($k > 10^9 M^{-1} \text{sec}^{-1}$). Cd²⁺ ions which react with e_t^- produce Cd⁺ ions in the bulk of the glasses. This is demonstrated by the subsequent second-order decay of Cd⁺. Cd²⁺ ions which react with the precursors of e_t^- produce Cd⁺ ions in the spurs. Such Cd⁺ ions decay away later by a process which is in agreement with the model of Schuler and coworkers. The fraction of Cd⁺ ions which is produced in the spurs increases with [Cd²⁺] in accordance with the competition scheme $e_m^- \rightarrow e_t^-$, $\text{Cd}^{2+} + e_m^- \rightarrow \text{Cd}^+$ where e_m^- represents a precursor of e_t^- . From the effect of [Cd²⁺] on the initial e_t^- and Cd⁺ absorptions, we found $k(e_m^- \rightarrow e_t^-)/k(\text{Cd}^{2+} + e_m^-) = (0.24 \pm 0.02) M$. Results are also reported for the recombination of Cd⁺ and the molar absorptivities of Cd⁺ and similar cations in aqueous solution.

Introduction

A mixture of two parts of ethylene glycol with one part of water yields upon cooling to the temperature range 123–193 K a transparent glassy ice. It has been found that in this medium, a trapped electron, e_t^- , is produced,^{1–3} with $G = 1.5 \pm 0.5$,¹ and optical absorption in the visible, peaking at 530 nm (at 70% ethylene glycol). Upon illumination

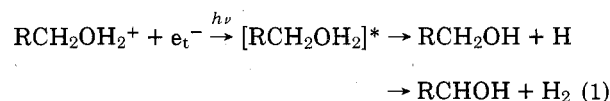
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Acknowledgment. The authors wish to thank C. A. Walker for his continuous help and valuable discussions during the experiments.

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in the visible, e_t^- is gradually converted to an alcohol radical according to the process



Addition of solutes could decrease the yield of e_t^- .^{1–3} This was interpreted as due to the reactions of scavengers with the precursors of e_t^- . Thus, Steen et al.³ found that a mobile electron, which they called e_m^- , was a precursor of