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Electrooxidation of Iodine on Smooth Platinum in Acetic Anhydride Medium

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Iodine in acetic anhydride gives two successive anodic voltammetric waves on smooth platinum. The first wave is due to the electrooxidation of I_2 to I^+ . The second anodic wave exhibits a limiting current which decreases progressively with the rest time of the electrode at a given constant potential tending to an asymptotic value, owing to the adsorption of electrode products. By use of a pulse-polarographic technique applicable to solid electrodes, it was possible to ascertain that the second anodic step is due to the overall electrode process $I^+ \rightarrow I^+$. The electrolysis of an iodine solution in acetic anhydride, carried out at the half-wave potential of the second anodic step of I_2 , shows that at this potential both iodine and acetic anhydride are electrooxidized. The oxidation of the solvent yields some red-brown condensation products of $(CH_3CO)_2O$ which are electrooxidized on platinum in the same potential range corresponding to the second anodic wave of iodine, giving rise to a well defined anodic pulse-polarogram. These condensation products are slowly iodinated by the iodine present in the solution.

A STUDY of the voltammetric behavior of iodine in acetic anhydride on smooth platinum was carried out for the first time by Plichon *et al.* (1) by the use of a rotating electrode. Subsequently, the authors (2) examined the two partial oxidation waves of I^- to I_3^- and to I_2 in acetic anhydride from a quantitative point of view, determining the instability constant $K = [I_2][I^-]/[I_3^-]$ of triiodide ion in this solvent. The aim of the present work is to describe the results of a study of the electrooxidation of I_2 in acetic anhydride on smooth platinum. This study has been carried out by adopting, as in the preceding paper, a platinum microelectrode with periodical renewal of the diffusion layer (DLPRE), used both in connection with a conventional polarograph (technique I) (3) and in connection with a pulse-polarographic system devised by the authors (technique II) (4).

EXPERIMENTAL

For the recording of voltammetric and pulse-polarographic curves the same equipment as in the preceding paper was adopted. The potential of the indicator electrode (DLPRE) was controlled *vs.* a Ag/AgCl, 0.3M LiCl (CH_3COOH) reference electrode. The acetic anhydride (Merck, unaffected by chromic acid) was purified by fractional distillation.

RESULTS AND DISCUSSION

Iodine in acetic anhydride yields two cathodic waves on platinum (the former due to its reduction to I_3^- and the latter to its successive reduction to I^-) as well as two anodic waves. Figure 1 shows the two anodic waves as recorded on the DLPRE with technique I. These waves are perfectly anal-

ogous to those obtained by Plichon *et al.* (1) on a rotating platinum electrode. The first anodic step, characterized by a height practically equal to the sum of the heights of the two cathodic steps, is due to the electrooxidation of I_2 to I^+ (under the form of the colorless species CH_3COOI). In fact, coulometric measurements performed by Plichon *et al.* (1) at the plateau of the first anodic wave of I_2 reveal that the almost complete decoloration of an iodine solution requires the passage of about two Faradays per mole of iodine through the electrolysis cell. An oscillographic investigation of the potentiostatic current-time curves, as recorded with technique I at the plateau of the anodic wave $I_2 \rightarrow I^+$, shows that the time dependence of these curves satisfies the Cottrell equation corrected for sphericity. Therefore the oxidation of I_2 to I^+ is diffusion-controlled. The second anodic wave of I_2 in $(CH_3CO)_2O$ exhibits several properties in common with the unique anodic wave of iodine in CH_3COOH examined in the preceding paper. Thus the second oxidation wave of I_2 in $(CH_3CO)_2O$, which in the current-potential curve of Figure 1 (recorded at a rate of polarization of 0.47 mV/sec) is about twice as high as the first anodic wave, increases with an increase in the rate of polarization. Furthermore, the mean limiting current, as recorded with technique I at a given constant potential, decreases progressively with the rest time of the electrode at such a potential, approaching gradually a constant value. Simultaneously the corresponding potentiostatic current-time curve as measured between two successive washings with technique I shows an increasing departure from the behavior described by the Cottrell equation. The potentiostatic current-time curves given by iodine in acetic anhydride at the plateau of the second anodic wave and recorded with technique II under experimental conditions identical to those in Figure 3 of the preceding paper, exhibit a behavior perfectly analogous to that encountered in CH_3COOH . This behavior can therefore be justified by the same arguments put forward for acetic acid, assuming adsorption of oxidation products of iodine at the electrode surface.

Here, too, the use of technique II allows the influence of this adsorption to be eliminated almost totally through a long enough pretreatment of the electrode at a sufficiently negative potential E_i prior to the application of the pulse $\Delta E = E_f - E_i$. Figure 2 shows the charge-potential curve given by $10^{-3}M$ I_2 and 0.3M LiClO₄ in $(CH_3CO)_2O$ for an initial period t_i equal to 90 sec and a final period t_f equal to 3 sec. The value of the initial potential E_i to which the electrode is continuously brought back during the period t_i equals +1.57 V. From the figure it is apparent that the second anodic wave is about four times higher than the first one. Furthermore, the instantaneous potentiostatic current flowing during t_f at the plateau of the second anodic wave of Figure 2 is diffusion-controlled. The preceding experimental findings lead to the conclusion that the second oxidation wave of I_2 in $(CH_3CO)_2O$ is due to the overall oxidation process $I^+ \rightarrow I^+$. The main difference between the behavior of iodine toward electrooxidation in CH_3COOH and in $(CH_3CO)_2O$ is, there-

(1) V. Plichon, J. Badoz-Lambling, and G. Charlot, *Bull. Soc. Chim. Fr.*, **1964**, 287.

(2) R. Guidelli and G. Piccardi, *Anal. Lett.*, **1**, 779 (1968).

(3) D. Cozzi, G. Raspi, and L. Nucci, *J. Electroanal. Chem.*, **12**, 36 (1966).

(4) G. Piccardi and R. Guidelli, *Ric. Sci.*, **38**, 247 (1968).

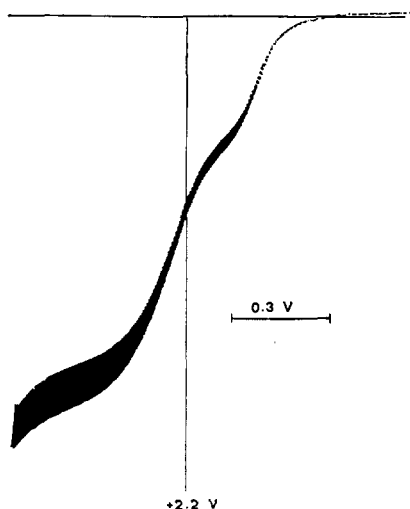


Figure 1. Anodic voltammogram of $10^{-3}M$ I_2 and $0.3M$ $LiClO_4$ in acetic anhydride as recorded on the DLPRE with technique I

$t_1 = 4$ sec; $t_w = 30$ msec

fore, represented by the fact that this latter solvent stabilizes the species with oxidation number +1. Thus, the anodic voltammograms given by iodine in mixtures of acetic anhydride and acetic acid exhibit two distinct steps up to ratios of CH_3COOH to $(CH_3CO)_2O$ of about 90% in volume.

The rising portion of the second step of the anodic charge-potential curve of I_2 in $(CH_3CO)_2O$ is appreciably drawn out on the potential axis ($E_{3/4} - E_{1/4} \sim 150$ mV), thus revealing the irreversible nature of the electrode process $I^I \rightarrow I^V$. From an analysis of this rising portion, carried out by the use of Equation 7 in the preceding paper, it has been possible to derive the value of the dimensionless parameter $\lambda = k_2 t_f^{1/2} / D^{1/2}$ as a function of E_f . The perfect linearity of the plot of $\log \lambda$ vs. E_f shows that the electrode process $I^I \rightarrow I^V$ is characterized by the presence of only one rate-determining charge-transfer step. The value 0.45 for $(n_0/\nu_1 +$

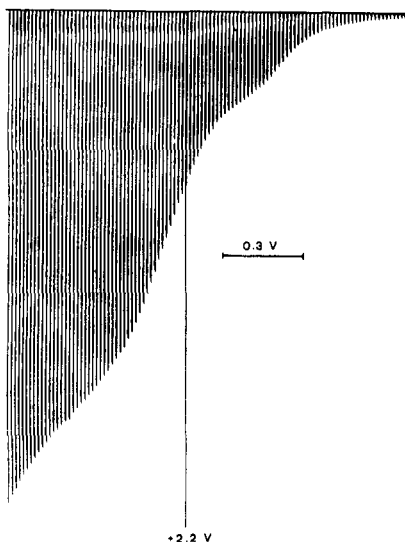


Figure 2. Anodic charge-potential curve of $10^{-3}M$ I_2 and $0.3M$ $LiClO_4$ in acetic anhydride

$t_i = 90$ sec; $t_f = 3$ sec; $E_i = +1.57$ V

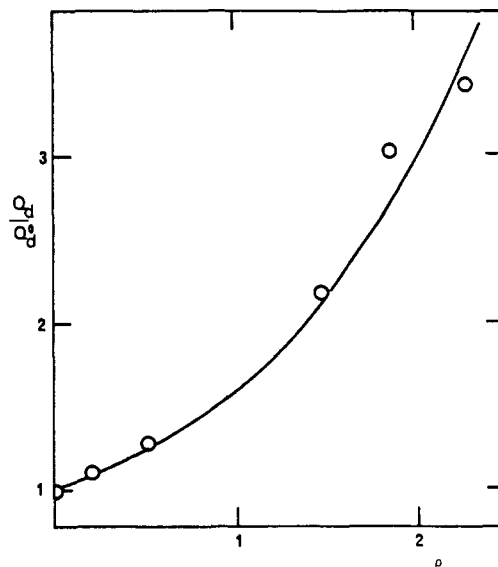


Figure 3. Plot of Q_d/Q_d^0 vs. ρ , as obtained from a $10^{-3}M$ solution of I_2 in $(CH_3CO)_2O$

$n_1\alpha)$, as derived from the slope of the above plot, suggests that $n_0 = 0$, $n_1 = 1$, and $\alpha = 0.45$. The rate-determining step for the overall electrode process $I^I \rightarrow I^V$ can therefore be schematically expressed by the equation:

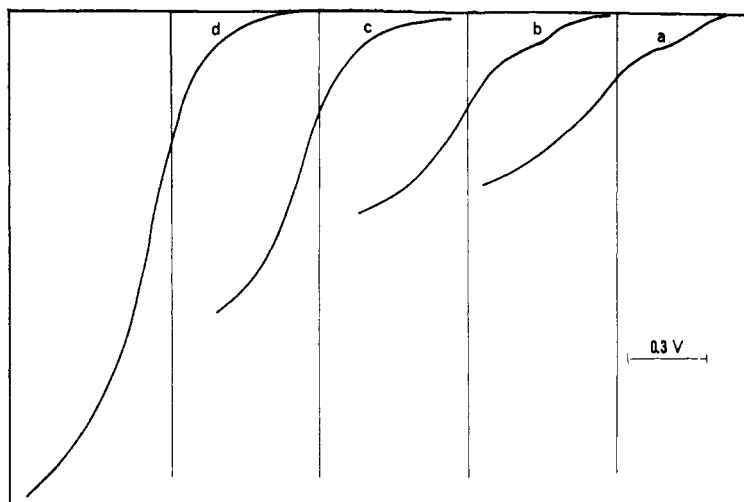


COULOMETRIC MEASUREMENTS

As opposed to what was done in acetic acid, it has not been possible to confirm the number of electrons involved in the second oxidation step of I_2 in $(CH_3CO)_2O$ by the coulometric method. The coulometric measurements were carried out as usual by electrolyzing 50 cm³ of $10^{-3}M$ I_2 in $(CH_3CO)_2O$ directly in the cell of the DLPRE on a platinum macroelectrode with an area of 12.5 cm², at the half-wave potential ($E_{1/2} = 2.28$ V) of the second anodic wave. The electrolysis on the macroelectrode was interrupted periodically to allow the recording of the anodic charge-potential curve of iodine on the DLPRE. Figure 3 shows the ratio Q_d/Q_d^0 between the height Q_d of the overall anodic charge-potential curve and its initial value Q_d^0 against the ratio ρ of the coulombs that have flowed through the cell to those theoretically required for the oxidation of the iodine originally contained in the cell up to the oxidation number +1. From the figure, it is apparent that, upon increasing the number of coulombs, the height of the overall anodic charge-potential curve increases rapidly, instead of decreasing according to expectations. Contemporaneously with this increase in the overall charge-potential curve, the first anodic step, due to the process $I_2 \rightarrow I^I$, tends to decrease up to its disappearance. This is clearly shown in Figure 4, where the anodic charge-potential curves recorded after having electrolyzed a $10^{-3}M$ iodine solution in $(CH_3CO)_2O$ for a sufficiently long period of time are characterized by the presence of only one step, with a half-wave potential very near to that of the second anodic step given by a nonelectrolyzed solution of I_2 in the same solvent. During the coulometric measurements, variously electrolyzed portions of the iodine solution were drawn from the cell and examined spectrophotometrically in the UV-visible. It was thus possible to observe that the adsorption peak given by iodine at the wavelength $\lambda_{max} = 362$ nm decreases gradually with the number of coulombs that have flowed through

Figure 4. Charge-potential curves of $10^{-3}M$ I_2 and $0.3M$ $LiClO_4$ in acetic anhydride, as recorded at the DLPRE after having electrolyzed the solution at $+2.28$ V with 0 (curve a), 0.055 (curve b), 0.16 (curve c), and 0.24 coulomb/cm² (curve d)

$t_i = 90$ sec; $t_f = 3$ sec; $E_i = +1.57$ V. Vertical lines refer to $+2.2$ V



the cell, approaching zero simultaneously with the disappearance of the first anodic step. It follows that the charge-potential curve given by an iodine solution in $(CH_3CO)_2O$, which has been sufficiently electrolyzed, is not attributable to the electrooxidation of iodine. The electrolysis of an iodine solution in $(CH_3CO)_2O$ at the potential $E = +2.28$ V initially produces the decoloration of the solution as a consequence of the disappearance of iodine and subsequently the appearance of a yellow color which changes progressively to red-brown. As the solution stands, it tends to deposit some brown tar. The oscillographic investigation of the potentiostatic instantaneous limiting currents recorded with technique II under the experimental conditions of Figure 4 reveals that these currents obey the Cottrell equation and are therefore diffusion-controlled. If, nevertheless, the period t_i preceding the pulse $\Delta E = E_f - E_i$ is made too short (say, a few seconds), then the potentiostatic instantaneous limiting currents undergo a progressive decrease and a deviation from the behavior expressed by the Cottrell equation, just as the curves of Figure 3 in the preceding paper. This explains why the coulometric measurements carried out by Plichon *et al.* (1) at a potential slightly more positive than the half-wave potential of the second anodic step of I_2 in $(CH_3CO)_2O$ lead to results somewhat different from those reported herein. Plichon (1) observes that the passage of a number of coulombs greater than that required for the oxidation of iodine up to the oxidation number $+7$ yields only a slight decrease in the

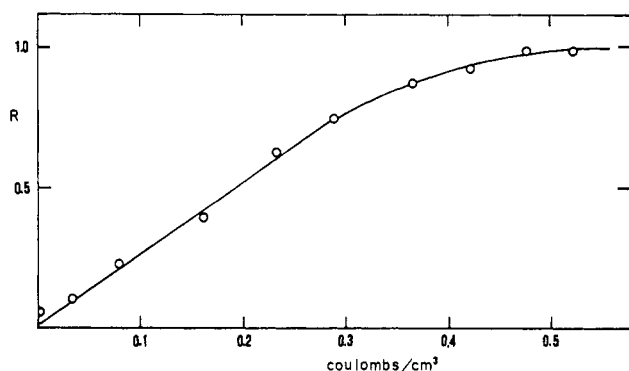


Figure 5. Plot of ratio R between the height of the charge-potential curves of variously electrolyzed solutions of $0.3M$ $LiClO_4$ in acetic anhydride and the asymptotic value of this height vs. the number of coulombs/cm² employed in the electrolysis

overall anodic voltammogram recorded at a rotating platinum electrode. Such a slight decrease has also been observed by us on the DLPRE when employing technique I. The differences between the behaviors observed with techniques I and II must be attributed to the adsorption of electrolysis products, the use of technique II eliminating in this case too the effects of such an adsorption.

The apparently anomalous results of the coulometric measurements carried out with iodine solutions in $(CH_3CO)_2O$ have been clarified by performing the electrolysis of the solvent containing $0.3M$ $LiClO_4$ in the absence of iodine on a platinum macroelectrode at a potential of $+2.4$ V. At this potential the residual current due to the oxidation of the solvent, as recorded on the DLPRE, is relatively negligible with respect to the current due to the oxidation of $10^{-3}M$ I_2 , although it is appreciable in an absolute sense. The electrolysis of $0.3M$ $LiClO_4$ in $(CH_3CO)_2O$ at the potential $E = +2.4$ V on the platinum macroelectrode was interrupted periodically in order to permit the recording of the anodic charge-potential curves given on the DLPRE by variously electrolyzed solutions. It was thus possible to observe that the electrolysis of the solvent containing only the supporting electrolyte is accompanied by the appearance of an anodic charge-potential curve whose height increases with the number of coulombs that have flowed through the cell. The height of this wave is initially proportional to the number of coulombs employed in the electrooxidation of the solvent, subsequently approaching a constant value (see Figure 5). The solvent alone, if electrolyzed for a sufficiently long period of time, turns yellow and finally red-brown just as a solution of I_2 in $(CH_3CO)_2O$. The half-wave potential of the anodic charge-potential curve given by the electrolyzed solvent is near to the half-wave potential of the second anodic wave given by I_2 in $(CH_3CO)_2O$, as appears from Figure 6, which shows a series of charge-potential curves obtained from variously electrolyzed solutions of $0.3M$ $LiClO_4$ in $(CH_3CO)_2O$. The oscillographic investigation of the potentiostatic instantaneous limiting currents as recorded with technique II under the experimental conditions of Figure 6 reveals that these currents are diffusion-controlled, provided the initial period t_i is kept above a certain minimum value.

The anodic charge-potential curves previously described must be attributed to the oxidation of acetic anhydride, which leads to the formation of acetoxyl radicals and acetylium ions (5), according to the equation:

(5) W. B. Mather and F. C. Anson, *ANAL. CHEM.*, **33**, 1634 (1961).

Figure 6. Charge-potential curves of 0.3M LiClO₄ in acetic anhydride, as recorded at the DLPRE after having electrolyzed the solution at +2.4 V with 0 (curve a), 0.08 (curve b), 0.16 (curve c), 0.23 (curve d), 0.37 (curve e), and 0.52 coulomb/cm² (curve f)

$t_i = 90$ sec; $t_f = 3$ sec; $E_i = +1.57$ V. Vertical lines refer to +2.0 V

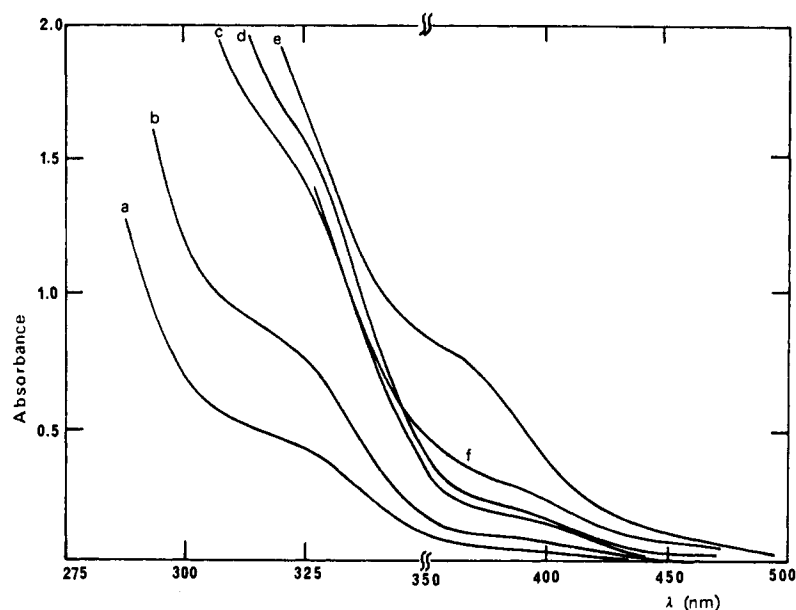
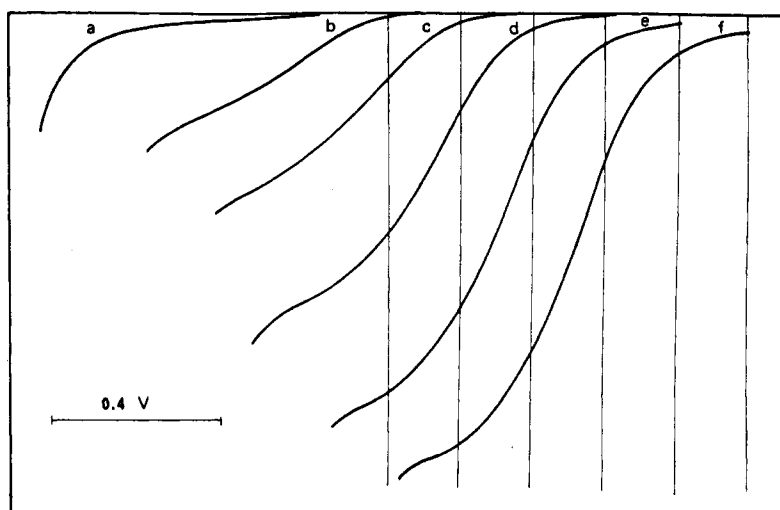
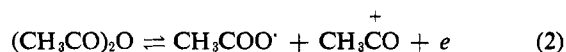
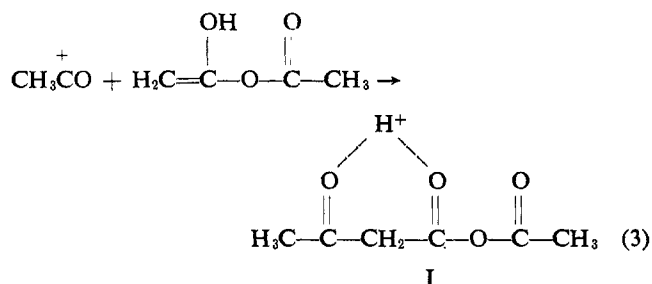


Figure 7. Curves a, b, c, and d are the UV-visible spectra of a 0.3M solution of LiClO₄ in (CH₃CO)₂O, electrolyzed with 0.23, 0.29, 0.48, and 0.52 coulomb/cm², respectively. Curves e and f are the spectra given by the most electrolyzed 0.3M LiClO₄ solution, immediately after the addition of 10⁻³M I₂ and six hours later, respectively



While the acetoxy radicals decompose very rapidly into methyl radicals and carbon dioxide, the acetylum ions tend to condense with the enol form of acetic anhydride as follows:



The product I is a relatively weak acid, which can further react with acetylum ions giving rise to higher condensation products. These condensation products are red-brown, which explains the red color assumed by (CH₃CO)₂O after a sufficiently long electrolysis. The anodic charge-potential curve given by electrolyzed solutions of LiClO₄ in (CH₃CO)₂O must therefore be attributed to the electrooxidation both of the product I and of eventual higher condensation products,

which consequently reveal themselves more easily oxidizable than the uncondensed acetic anhydride. In the first stages of the electrolysis of the solvent, the yield of the electrode Reaction 2 is near unity, so that the amount of the product I which forms is practically proportional to the number of coulombs that have flowed through the electrolysis cell. It follows that the height of the anodic charge-potential curve given by the electrolyzed solution increases proportionally to the number of coulombs employed in the electrolysis, as appears from Figure 5. As electrolysis proceeds, an increasing fraction of the current flowing through the macroelectrode is consumed in the electrooxidation of the condensation products of acetic anhydride. It follows that the concentration of these latter products, and consequently the height of the anodic charge-potential curve, show a lower rate of increase. The preceding interpretation of the anodic charge-potential curves in Figure 6 has been confirmed by recording the charge-potential curve given by a solution of acetylum perchlorate in (CH₃CO)₂O, prepared according to Mather and Anson (5). The solution of CH₃CO ClO₄⁺ in (CH₃CO)₂O tends to turn rapidly red-brown, as a consequence of the formation of condensation products of the type I. The charge-potential curve given by an already brown solution

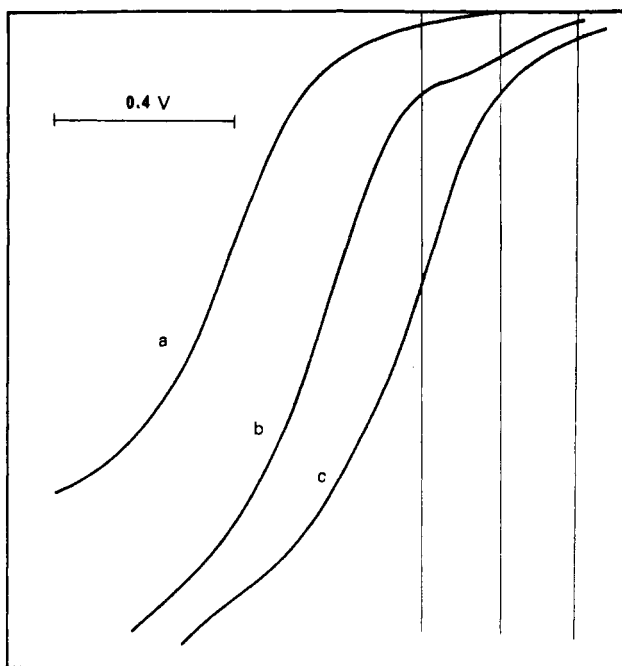


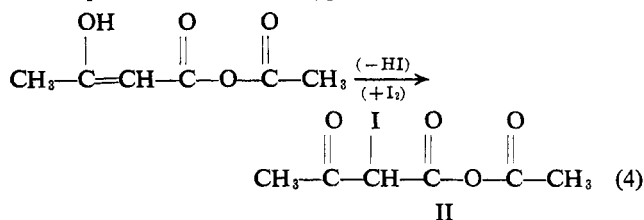
Figure 8. Curve *a* is the charge-potential curve of a 0.3*M* solution of LiClO_4 in acetic anhydride, electrolyzed with 0.52 coulomb/ cm^3 . Curves *b* and *c* are the charge-potential curves given by the same solution, immediately after the addition of $10^{-3}M$ I_2 and six hours later, respectively

$t_i = 90$ sec; $t_f = 3$ sec; $E_i = 1.57$ V. Vertical lines refer to +2.0 V

of $10^{-3}M$ $\text{CH}_3\text{CO}^+\text{ClO}_4^-$ and of 0.3*M* LiClO_4 in $(\text{CH}_3\text{CO})_2\text{O}$ is identical to those in Figure 6. Furthermore, its height is near that of the charge-potential curve obtained by electrolyzing a 0.3*M* solution of LiClO_4 in $(\text{CH}_3\text{CO})_2\text{O}$ with the number of coulombs theoretically necessary to create a $10^{-3}M$ concentration of acetylum ions according to the electro-oxidation Reaction 2.

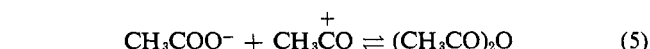
Upon introducing I_2 either in a previously electrolyzed solution of LiClO_4 in $(\text{CH}_3\text{CO})_2\text{O}$ or in a solution of $\text{CH}_3\text{CO}^+\text{ClO}_4^-$ in $(\text{CH}_3\text{CO})_2\text{O}$, the iodine reacts slowly with the condensation products of $(\text{CH}_3\text{CO})_2\text{O}$ contained therein. This is clearly shown in Figure 7, in which the curves *a*, *b*, *c*, and *d* are the UV-visible spectra of a 0.3*M* solution of LiClO_4 in $(\text{CH}_3\text{CO})_2\text{O}$, electrolyzed with 0.23, 0.29, 0.48, and 0.52 coulombs/ cm^3 , respectively. If the most highly electrolyzed solution of LiClO_4 is made $10^{-3}M$ in I_2 and the spectrum of the solution so obtained is recorded immediately after, curve *e* in Figure 7 is obtained, in which the adsorption peak of iodine is superimposed on the spectrum because of the condensation products of $(\text{CH}_3\text{CO})_2\text{O}$. As the solution stands, however, the peak of iodine gradually disappears. In practice, after six hours at room temperature, the solution is perfectly stabilized and yields spectrum *f* in Figure 7, which is similar to that of the electrolyzed solution not containing iodine. In the stabilized solution so obtained "inorganic" iodine (*i.e.*, iodine not bound by covalent bonds within organic molecules) was sought by us. For this purpose the above solution was diluted with water. Subsequently, sodium bisulfite was added in order to reduce all the "inorganic" iodine eventually present to iodide. After having removed SO_2 with nitrogen gas, AgNO_3 was added to the solution without observing any appreciable turbidity. The same experiment, carried out with solutions of I^- , I_2 , or IO_3^- in $(\text{CH}_3\text{CO})_2\text{O}$ containing 10^{-4} g-atom of iodine per liter, gives rise to a clearly visible

turbidity. We must conclude that the reaction of I_2 with the condensation products of $(\text{CH}_3\text{CO})_2\text{O}$ does not produce "inorganic" iodine to an appreciable extent. Quite probably I_2 combines with the enol form of product I or of more condensed products of the same type:

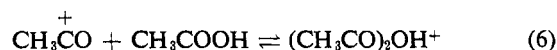


giving rise to product II or to analogous products with higher molecular weights. In acetic anhydride medium the hydrogen iodide produced in Reaction 4 is probably in a condition to combine with the carbonyl groups present in the condensation products of $(\text{CH}_3\text{CO})_2\text{O}$, giving rise to more iodinated products. Figure 8 shows the charge-potential curve given by a 0.3*M* solution of LiClO_4 in $(\text{CH}_3\text{CO})_2\text{O}$ electrolyzed with 0.52 coulomb/ cm^3 (curve *a*), as well as the charge-potential curve given by the same solution immediately after the addition of $10^{-3}M$ I_2 (curve *b*). Curve *b* shows a first anodic step due to the oxidation of I_2 to I^+ . The second oxidation wave of I_2 , due to the electrode process $\text{I}^+ \rightarrow \text{I}^{IV}$, merges with the wave given by the condensation products of $(\text{CH}_3\text{CO})_2\text{O}$. Curve *c* in Figure 8 represents the charge-potential curve given by the same solution which gives curve *b*, after having waited for stabilization. In curve *c*, the anodic step due to the oxidation of I_2 to I^+ does not appear.

In light of the preceding experimental findings, the increase in the height of the anodic charge-potential curve given by I_2 in $(\text{CH}_3\text{CO})_2\text{O}$ following the electrolysis of the solution at the potential $E = +2.28$ V (Figures 3 and 4) can be explained by the simultaneous oxidation at this potential both of iodine to I^{IV} and of acetic anhydride according to Reaction 2. In order to carry out coulometric measurements suitable for the determination of the number of electrons involved in the overall oxidation of iodine in $(\text{CH}_3\text{CO})_2\text{O}$, we tried to prevent the condensation of acetic anhydride as a



whereas in the second case they are expected to be blocked by acetic acid according to the reaction:



Both in the presence of CH_3COONa and in the presence of CH_3COOH , the progressive increase in the number of coulombs that have flowed through the cell does not produce any longer an increase in the heights of the overall anodic charge-potential curves of I_2 , which heights remain, nevertheless, practically constant or decrease only slightly. In the same time the partial oxidation step of iodine to I^+ decreases gradually up to its extinction. We must therefore conclude that the addition of either CH_3COONa or CH_3COOH has only a limited effect on preventing the condensation of $(\text{CH}_3\text{CO})_2\text{O}$ by acetylum ions.

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