

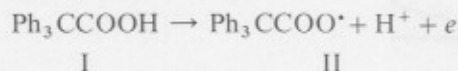
ON THE E.S.R. SPECTRA OF INTERMEDIATES GENERATED DURING THE ELECTROCHEMICAL OXIDATION OF TRIPHENYLACETIC ACID IN ACETONITRILE

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A recent brief report¹ of the electrochemical oxidation of triphenylacetic acid (I) in acetonitrile described the first direct observation of a radical intermediate in the Kolbe oxidation. An electron spin resonance (e.s.r.) signal of a primary electrode product was recorded while electrolyzing the acid in the cavity of an e.s.r. spectrometer. The thirteen-line spectrum that was observed was analyzed as hyperfine interaction with two *para*-protons ($a_p = 3.5 \pm 0.1$ G) and four *ortho*-protons ($a_o = 2.2 \pm 0.1$ G). On the basis of this analysis, the paramagnetic species was identified as the triphenylacetoxyl radical (II), a possible product from a one-electron oxidation of the triphenylacetic acid (I).



It seemed intriguing that any paramagnetic species containing the triphenylmethyl moiety would show coupling into only two of the three aromatic rings and, further, that such large long-range coupling constants had been observed. Also triphenylacetoxyl radical should undergo a very rapid decarboxylation to form the triphenylmethyl radical, a species that had been generated in this laboratory by the decomposition of phenylazotriphenylmethane and had been observed to be stable in



acetonitrile containing tetrabutylammonium perchlorate (TBAP). The e.s.r. spectrum obtained for the triphenylmethyl radical under these conditions ($a_p = 2.84$ G, $a_o = 2.58$ G, $a_m = 1.15$ G) was very dissimilar to that reported for the radical resulting from the Kolbe electrolysis^{1,*}.

These inconsistencies prompted a reexamination of this system as part of a general study of radical intermediates in electrochemical transformations². The development in this laboratory of an accurate cell for simultaneous electrochemical-electron spin resonance (s.e.e.s.r.)^{3,4} measurements has aided many such investigations

* Since the actual e.s.r. spectrum obtained by the Russian workers was not published, a spectrum was synthesized by computer techniques using the reported coupling constants and an arbitrary linewidth (400 mG) and then an attempt was made to simulate this spectrum using the coupling constants for the triphenylmethyl radical. Even with large linewidths (*i.e.*, poor resolution), the two spectra were distinctly different.

by allowing realistic potential control during *in situ* electrochemical generation of paramagnetic species in the e.s.r. cavity.

Previous studies of the Kolbe oxidation of triphenylacetic acid in nonaqueous media have involved use of methanol and acetic acid⁵ and of N,N-dimethylformamide (DMF)⁶ as solvents and were performed by electrolyzing at constant current with no potential control. The products isolated from methanol and acetic acid were triphenylmethyl methyl ether and triphenylmethyl acetate, respectively, and are consistent with the intermediacy of a triphenylmethyl carbonium ion.

The somewhat unusual products observed from the oxidation of triphenylacetic acid in DMF were rationalized by proposing a reaction of the solvent with triphenylacetoxyl radical⁶. Subsequent investigations using controlled potentials, however, have shown that analogous products may be formed by an initial oxidation of DMF followed by reaction with the carboxylate anion⁷. This possibility casts doubt on the previously proposed triphenylacetoxyl radical mechanism.

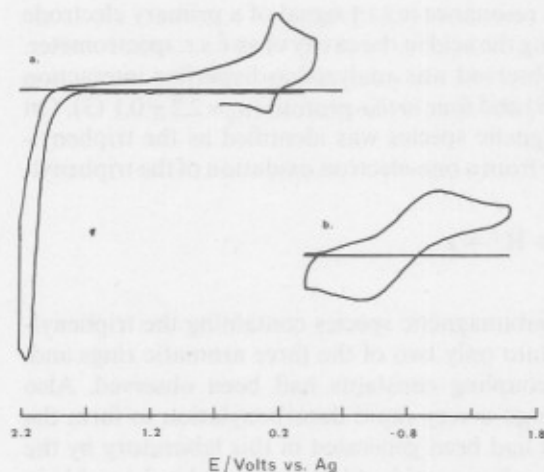


Fig. 1. Cyclic voltammogram of 1 mM triphenylacetic acid in acetonitrile containing 0.1 M TBAP at a platinum working electrode; scan rate, 200 mV s^{-1} . (a) Initial positive scan starting at 0.0 V; (b) initial negative scan starting at 0.0 V.

On cyclic voltammetry, triphenylacetic acid (1 mM) at a platinum anode in acetonitrile containing 0.1 M TBAP showed an irreversible oxidation peak at 2.11 V *vs.* Ag pseudo reference electrode which gave rise to a smaller reversible reduction peak at 0.20 V (Fig. 1a). Coulometry performed at 2.2 V *vs.* Ag in a pre-electrolyzed acetonitrile-TBAP solution 3.3 mM in triphenylacetic acid gave an *n* value of two for the oxidation. These data indicate a two-electron oxidation of the acid to triphenylmethyl carbonium ion which undergoes a reversible one-electron reduction to the triphenylmethyl radical at 0.20 V. This finding is not surprising in light of Ebersson's work⁸ which shows that Kolbe oxidations proceed via a two-electron process if the initially formed radical has an ionization potential less than 8 eV. The ionization potential for triphenylmethyl radical has been reported⁹ as 6.5 eV.

A 5.5 mM solution of triphenylacetic acid in acetonitrile containing 0.1 M TBAP

was oxidized at 2.0 V vs. a Ag pseudo reference electrode in the s.e.s.r. cell situated in the e.s.r. cavity. No signal was observed during the potential step; however, after open-circuiting the cell following a relatively long potential step (or a series of shorter potential steps), a signal appeared which increased in intensity with time. The spectrum shows seventeen lines and appears to be that for the triphenylmethyl radical with poor resolution. The spectrum may be closely computer simulated with a 190 mG linewidth using coupling constants ($a_p=2.846$, $a_o=2.58$ G, $a_m=1.15$ G) very close to those reported for triphenylmethyl radical in benzene¹⁰ (Fig. 2).

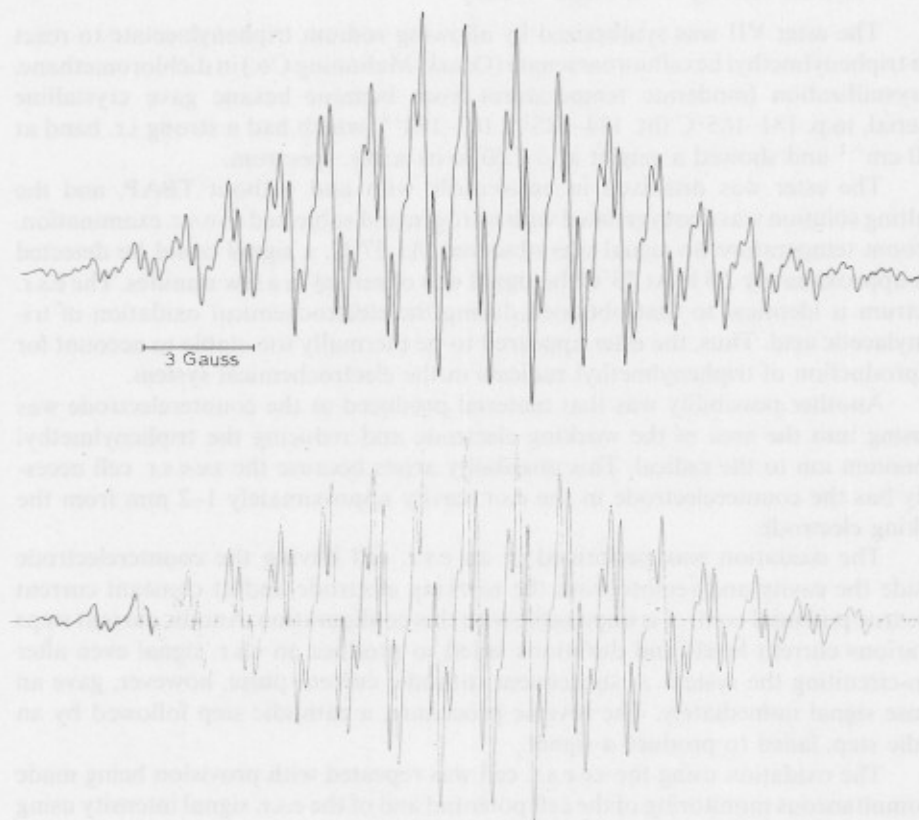
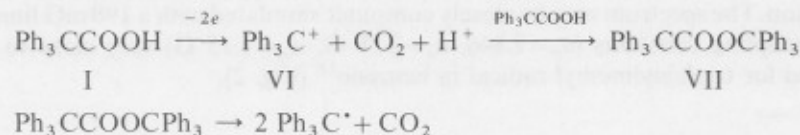


Fig. 2. E.s.r. spectrum obtained by *in situ* electrochemical oxidation of triphenylacetic acid. Top, experimental spectrum; bottom, computer-simulated spectrum, coupling constants, $a_1=2.84$ G, $a_2=2.58$ G, $a_3=1.15$ G; linewidth 190 mG.

A subsequent potential step to 2.0 V caused a rapid disappearance of the e.s.r. signal. Open-circuiting again produced the signal after an induction period, the length of which was an inverse function of the duration of the potential step.

One likely possibility was that some unstable intermediate was being formed by the primary non-paramagnetic electrogenerated species and that this intermediate subsequently underwent a slow thermal decomposition to give triphenylmethyl radicals. The most reasonable mechanism appeared to be a two-electron oxidation

of the triphenylacetic acid (I) to give triphenylmethyl carbonium ion (VI), carbon dioxide, and a proton, followed by reaction of the carbonium ion with the starting acid to form triphenylmethyl triphenylacetate (VII). This ester was expected to be thermally unstable and could homolytically decompose to yield detectable amounts of triphenylmethyl radicals*.



The ester VII was synthesized by allowing sodium triphenylacetate to react with triphenylmethyl hexafluoroarsenate (Ozark-Mahoning Co.) in dichloromethane. Recrystallization (moderate temperature) from benzene-hexane gave crystalline material, m.p. 181–185°C (lit. 184–185¹³, 183–184¹⁴) which had a strong i.r. band at 1740 cm⁻¹ and showed a singlet at δ 7.20 in its n.m.r. spectrum.

The ester was dissolved in acetonitrile with and without TBAP, and the resulting solution was deoxygenated with nitrogen and subjected to e.s.r. examination. At room temperature no signal was observed. At 57°C, a signal could be detected after approximately 2.5 h. At 75°C the signal was observed in a few minutes. The e.s.r. spectrum is identical to that obtained during the electrochemical oxidation of triphenylacetic acid. Thus, the ester appeared to be thermally too stable to account for the production of triphenylmethyl radicals in the electrochemical system.

Another possibility was that material produced at the counterelectrode was diffusing into the area of the working electrode and reducing the triphenylmethyl carbonium ion to the radical. This possibility arises because the s.e.e.s.r. cell necessarily has the counterelectrode in the e.s.r. cavity approximately 1–2 mm from the working electrode.

The oxidation was performed in an e.s.r. cell having the counterelectrode outside the cavity and remote from the working electrode and at constant current since true potential control is impossible with this configuration. Anodic current steps of various current levels and durations failed to produce an e.s.r. signal even after open-circuiting the system. A subsequent cathodic current pulse, however, gave an intense signal immediately. The reverse procedure, a cathodic step followed by an anodic step, failed to produce a signal.

The oxidation using the s.e.e.s.r. cell was repeated with provision being made for simultaneous monitoring of the cell potential and of the e.s.r. signal intensity using a dual-pen strip chart recorder. This allowed monitoring of the rest potential of the cell during the open-circuit period following a potential step. Upon breaking the circuit after a potential step to 2.0 V, the rest potential immediately shifted, usually in

* The energy of activation for generation of triphenylmethyl radicals from triphenylmethyl triphenylacetate would be no more than *ca.* 49 kcal mol⁻¹ and is expected to be considerably less. The higher limit is derived from the measured carbon-carbon bond dissociation energy of diphenylacetic acid¹¹ (52 kcal mol⁻¹), the expectation that an ester of this acid would have a comparable carbon-carbon bond strength, and the decrease in energy anticipated from the greater stabilities of tertiary as compared to secondary radicals. Factors that could contribute to a lowering of the bond dissociation energy include release of steric strain as a result of the rehybridization that accompanies bond cleavage and the exothermicity of formation of carbon dioxide associated with development of a transition state for molecular decomposition in which not only carbon-carbon but also carbon-oxygen bond rupture is occurring¹².

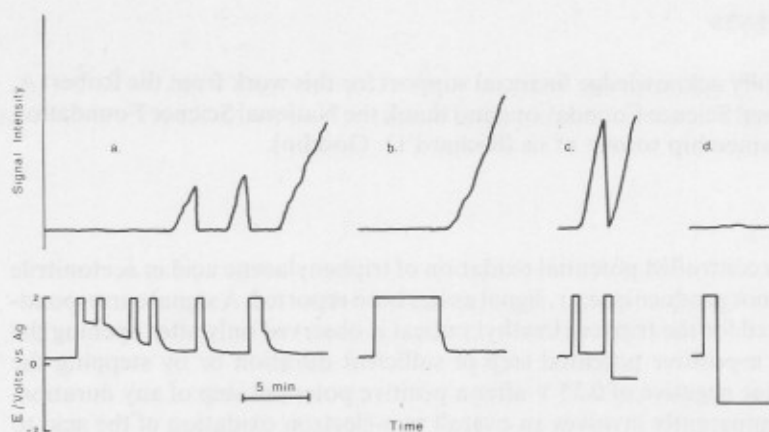


Fig. 3. E.s.r. signal intensity as a function of the s.e.e.s.r. cell potential. (a, b) Initial potential step to 2.0 V followed by opening the circuit; (c) initial potential step to 2.0 V followed by a step to 0.3 V and -0.5 V; (d) initial potential step to 2.0 V followed by a step of -1.2 V.

an S-curve fashion, to a more negative potential (Fig. 3a, b). The final rest potential depended on the duration of the anodic step, being more negative with longer potential steps. During a series of short potential steps, the final rest potential initially became more positive for the first few steps and then became more negative with each subsequent step.

An e.s.r. signal was observed only when the rest potential became more negative than 0.35 V. This behavior implies that some reducing agent is present which brings the rest potential to that of the carbonium ion-radical couple. Supporting this hypothesis is the observation that if instead of opening the circuit after the 2.0 V step, the potential was stepped to a value negative of 0.35 V (Fig. 3c), a signal was produced even after an initial step of short duration.

If, however, the potential was stepped from 2.0 V to a value negative of -1.0 V (Fig. 3d), no signal was produced. This could possibly be due to the direct reduction of the triphenylmethyl carbonium ion to the triphenylmethide ion via two successive one-electron steps with no appreciable amount of radical being liberated. Cyclic voltammetry of triphenylacetic acid revealed a broad reduction peak at -0.97 V. This peak was present, however, even without first making an anodic scan (Fig. 1b). This cathodic peak may be due to the reduction of the acidic proton of triphenylacetic acid, and the peak corresponding to the reduction of the triphenylmethyl radical to the anion may be obscured by this reduction. The absence of an e.s.r. signal upon a second step to -1.0 V may be due to the electrochemical reduction of the carbonium ion described above or to the reduction of the carbonium ion by hydrogen produced by reduction of the acid.

In conclusion, our results indicate that the electrochemical oxidation of triphenylacetic acid in acetonitrile proceeds via an overall two-electron process (possibly occurring via two one-electron processes) to give the triphenylmethyl carbonium ion instead of a one-electron process to give a radical. No insight could be gained into the nature of the radical reported in the Russian work¹.

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SUMMARY

The *in situ* controlled potential oxidation of triphenylacetic acid in acetonitrile at platinum does not produce an e.s.r. signal as has been reported. A signal corresponding to that reported for the triphenylmethyl radical is observed only after opening the circuit following a positive potential step of sufficient duration or by stepping the potential to a value negative of 0.35 V after a positive potential step of any duration. The mechanism apparently involves an overall two-electron oxidation of the acid to produce triphenylmethyl carbonium ion and carbon dioxide. The carbonium ion may then be reduced to the radical electrochemically or by diffusion of reduced material from the nearby counterelectrode in the e.s.r. electrochemical cell.

REFERENCES

- 1 N. B. Kondrikov, V. V. Orlov, V. I. Ermakov and M. Ya. Fiochin, *Elektrokhimiya*, 8 (1972) 920.
- 2 A. J. Bard, J. C. Gilbert and R. D. Goodin, *J. Amer. Chem. Soc.*, 96 (1974) 620.
- 3 I. B. Goldberg and A. J. Bard, *J. Phys. Chem.*, 75 (1971) 3281; I. B. Goldberg and A. J. Bard, *ibid.*, 78 (1974) 290.
- 4 I. B. Goldberg, D. Boyd, R. Hirasawa and A. J. Bard, *J. Phys. Chem.*, 78 (1974) 295.
- 5 R. P. Linstead, B. R. Shephard and B. C. L. Weedon, *J. Chem. Soc.*, (1952) 3624.
- 6 L. Rand and A. F. Mohar, *J. Org. Chem.*, 30 (1965) 3156.
- 7 L. Ebersson and K. Nyberg, *J. Amer. Chem. Soc.*, 88 (1966) 1686.
- 8 L. Ebersson, *Acta Chem. Scand.*, 17 (1963) 2004.
- 9 R. S. Neale, *J. Phys. Chem.*, 68 (1964) 143.
- 10 D. B. Chesnut and G. J. Sloan, *J. Chem. Phys.*, 33 (1960) 637.
- 11 J. A. Kerr, *Chem. Rev.*, 66 (1966) 465.
- 12 J. P. Lorand and P. D. Bartlett, *J. Amer. Chem. Soc.*, 88 (1966) 3294.
- 13 R. Anschutz, *Ann.*, 359 (1908) 196.
- 14 H. Wieland and F. G. Fischer, *Ann.*, 446 (1926) 49.