

**ORGANIC REACTIVE INTERMEDIATES: X.  
PREPARATION OF AROMATIC CATION  
RADICALS BY THE USE OF DDQ IN  
TRIFLUOROACETIC ACID/  
DICHLOROMETHANE SOLVENT SYSTEM**

K. L. HANDOO and K. GADRU

Department of Chemistry, University of Kashmir,  
Srinagar 190 006, India.

ALTHOUGH a large body of knowledge concerning complexes of the charge transfer type between donor molecules and quinones as acceptors has accumulated over the years<sup>1</sup>, only a few reports exist on the fate of these complexes in acid medium<sup>2-4</sup>.

In the present study, we have found that in a number of cases, deep-coloured solutions are formed when electron-rich aromatic and heterocyclic molecules are allowed to react with high potential quinones, particularly, 2,3-dichloro-5,6-dicyano benzoquinone (DDQ) in dichloromethane containing a small amount of TFA. For example, on adding a few drops of TFA to a mixture of thianthrene ( $1.0 \times 10^{-4}$  M) and DDQ ( $0.5 \times 10^{-4}$  M) in  $\text{CH}_2\text{Cl}_2$  at room temperature ( $28^\circ$ ), the solution developed a purple colour almost instantaneously which gave strong EPR signals (figure 1a) and electronic absorption spectrum (figure 1b) that provide an unequivocal evidence for the formation of thianthrene cation radicals. Similarly, other electron-rich organic molecules of a wide range of oxidation potentials yielded the corresponding cation radicals whose electronic absorption spectra, in their own right, indicate cation radical formation. In figure 2, the visible absorption spectra of 9,10-dimethylantracene, ferrocene, biphenyl, tetrathiofulvalene and rubrene cation radicals, thus prepared in 7-10% TFA in  $\text{CH}_2\text{Cl}_2$  solvent system, are shown.

A remarkable feature of this work is the ready formation of cation radicals from a host of organic molecules whose solutions under these conditions show considerable stability. Another aspect is the ability of DDQ to initiate reactions in which initially formed cation radicals participate in further reactions. In the present study, we have, however, concentrated on the preparation of stable cation radicals. Eighteen substrates, out of a large number of organic compounds oxidisable by DDQ, are listed in table 1.

These reactions furnish an example of single electron transfer (ET), the concept of which is gaining popularity and guiding many current investigations on organic reactions<sup>5</sup>. One would question as to which species in the system (DDQ/TFA) acts as the one-

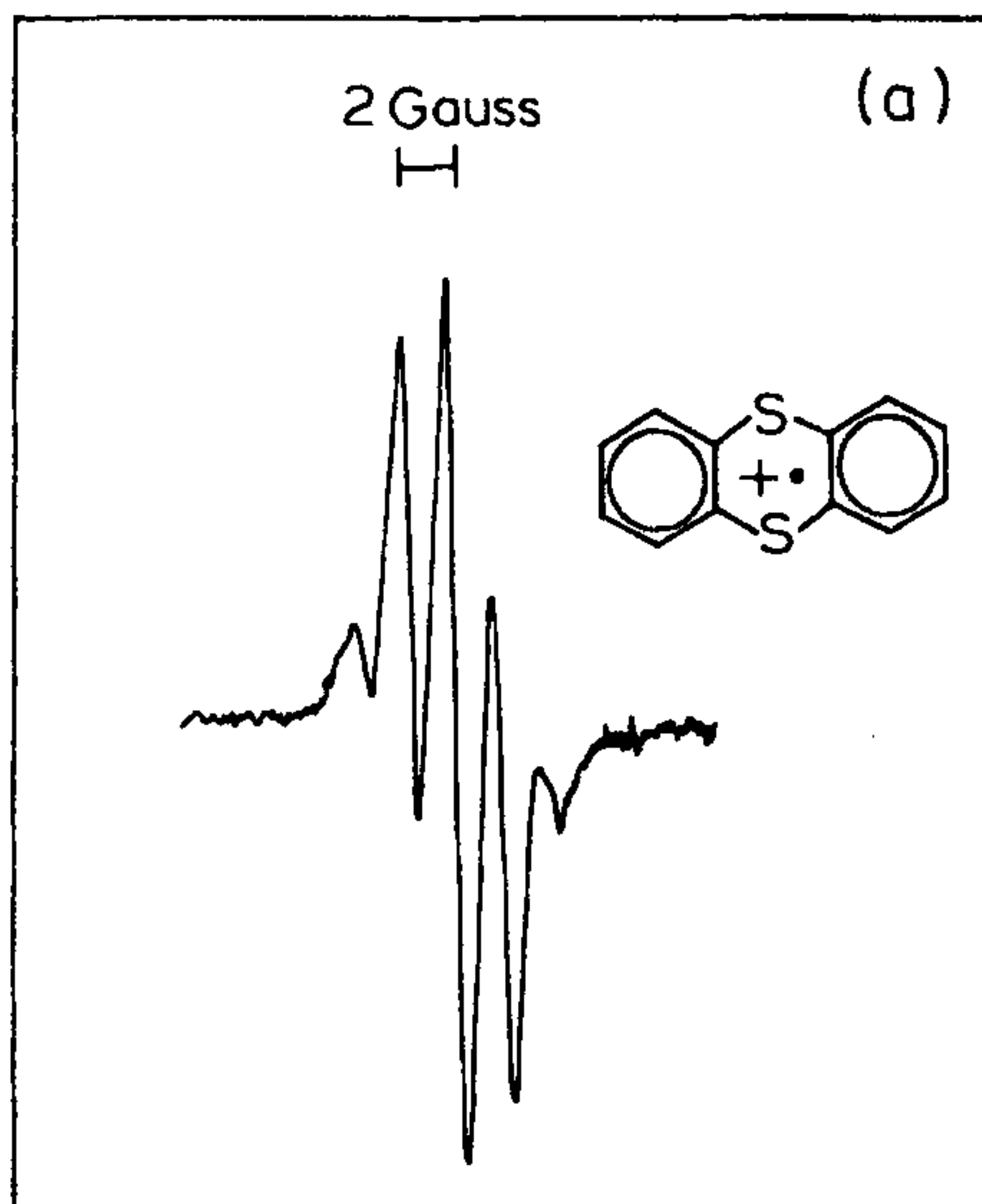
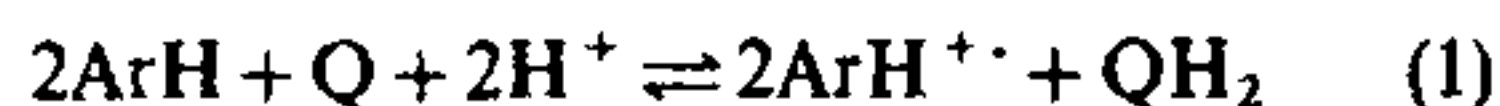
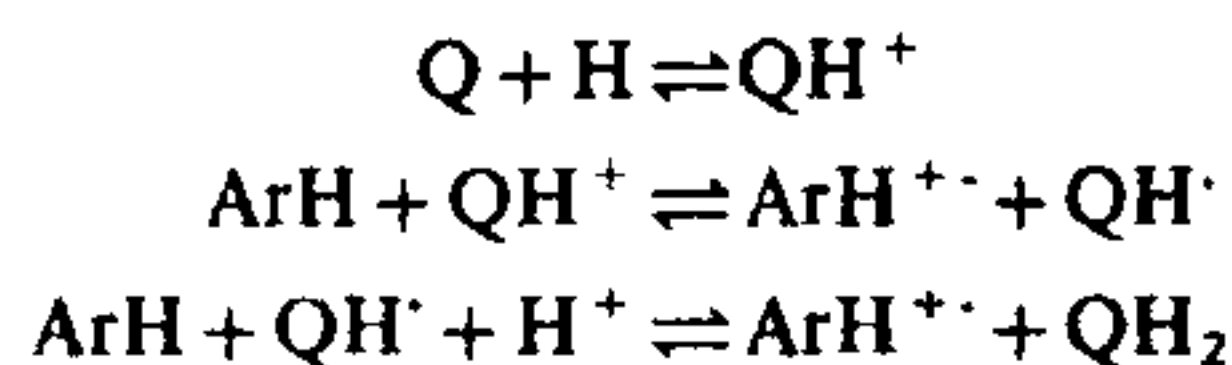
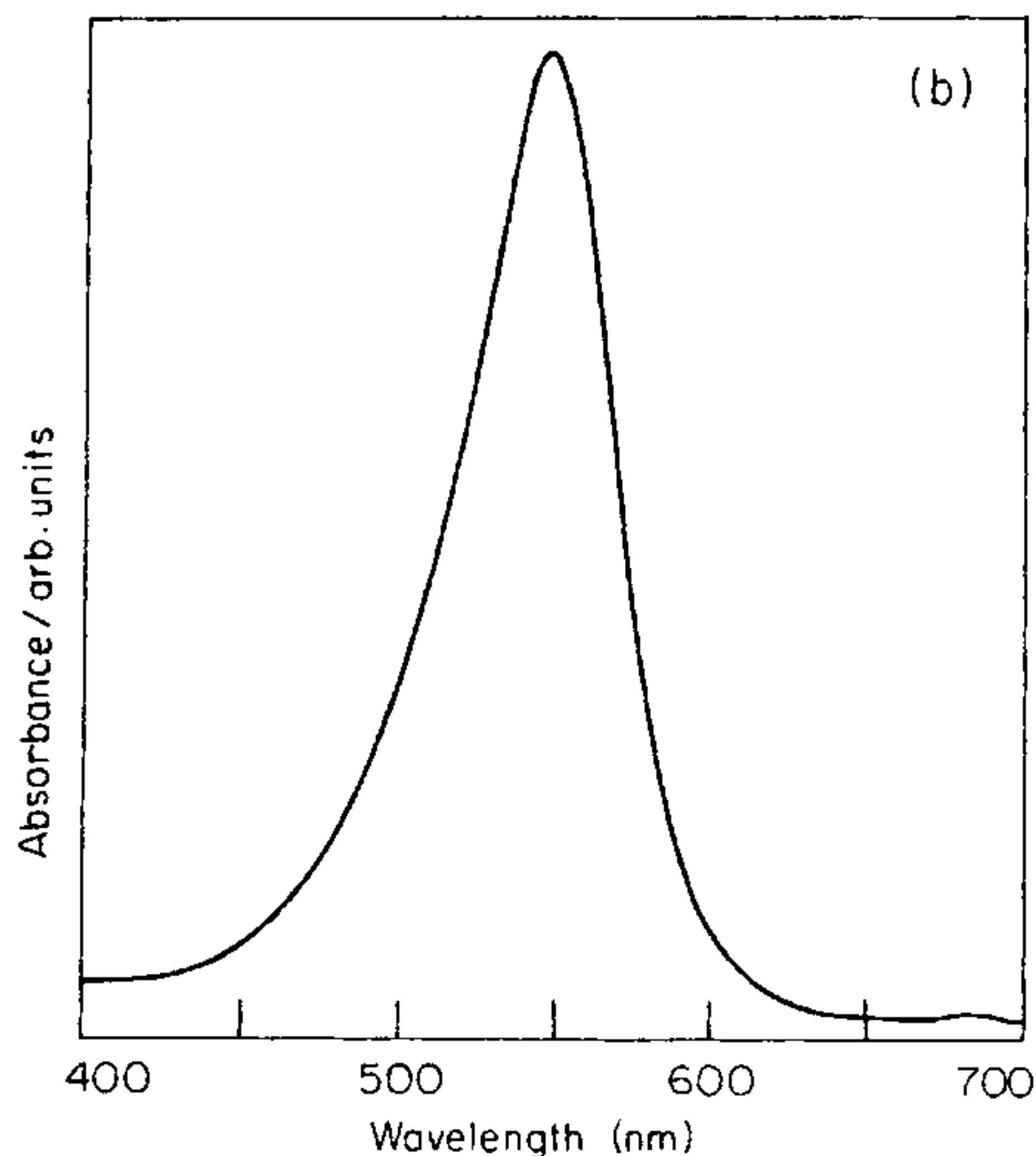


Figure 1a. EPR spectrum of thianthrene cation radical formed on oxidation of thianthrene with DDQ in TFA/ $\text{CH}_2\text{Cl}_2$  (1:10 v/v) solvent system at  $28^\circ\text{C}$ .

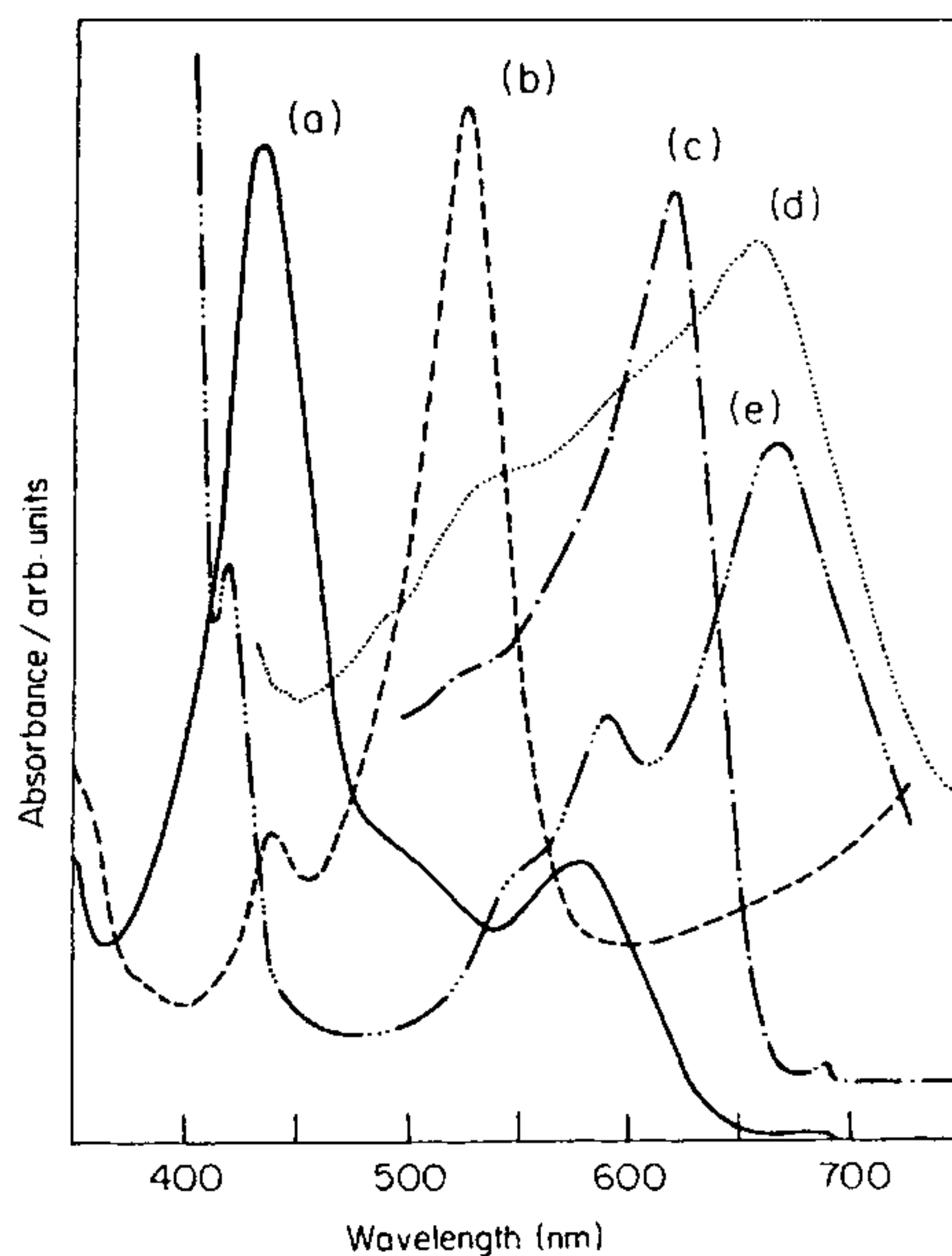
electron oxidant. A recent study<sup>6</sup> suggests that protonation of the oxidant, quinone (Q), occurs in the presence of the acid and it is the protonated quinone ( $\text{QH}^+$ ) that abstracts an electron from the substrate (ArH) (see equation (1))



Our studies, wherein stoichiometry based on spectrophotometric assaying of cation radicals was used to probe into the mechanism, account for the equilibrium presented in equation (1). We, however, believe that the active species is not the protonated quinone but the quinone itself which is dramatically activated by acids, particularly TFA, to act as the strong one-electron oxidant. Our arguments against  $\text{QH}^+$  as the pivotal species are as follows: (i) The electronegatively substituted quinones possess low basicity<sup>7,8</sup> to be susceptible to instant protonation by acids such as TFA;



**Figure 1b.** Visible absorption spectrum of thianthrene cation radical formed on oxidation of thianthrene with DDQ in TFA/CH<sub>2</sub>Cl<sub>2</sub> solvent mixture.



**Figure 2.** Visible absorption spectrum of cation radicals obtained by DDQ oxidation of (a) tetrathiofulvalene, (b) rubrene, (c) ferrocene, (d) biphenyl and (e) 9,10-dimethylantracene in TFA/CH<sub>2</sub>Cl<sub>2</sub> (1:10 v/v) solvent system at 28°C.

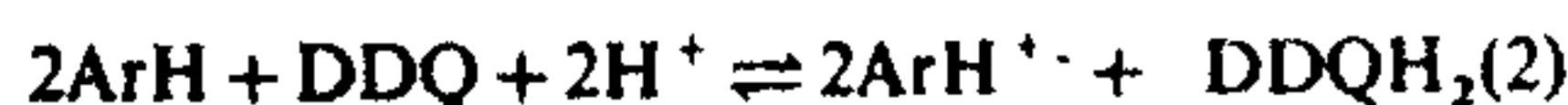
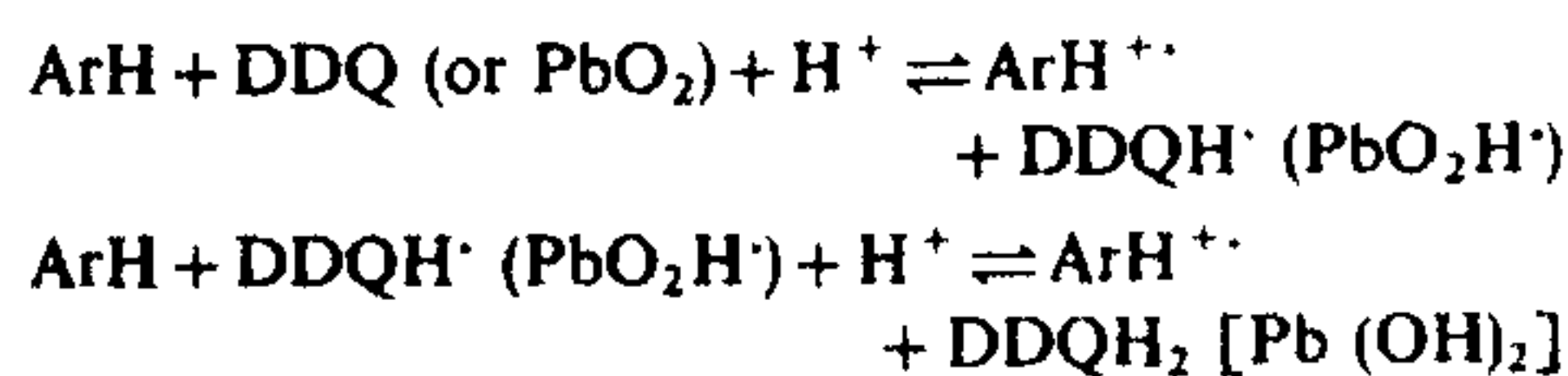
**Table 1**  $\lambda_{max}$  of cation radicals obtained by oxidation of the parent compound with DDQ in TFA at room temperature (28°).

Substrate <sup>+</sup>	Observed $\lambda_{max}$	Reported $\lambda_{max}$
Pyrene	505	505 <sup>a</sup>
Rubrene	525	<i>b</i>
Fluorene	532	<i>b</i>
Perylene	543	540 <sup>c</sup>
Acenaphthene	512	<i>b</i>
Anthracene	712	715 <sup>c</sup>
9,10-Dimethylantracene	669.5	<i>b</i>
9,10-Diphenylantracene	727, 652, 593	724, 653, 596 <sup>c</sup>
Naphthalene	535	535 <sup>d</sup>
Thianthrene	545	546 <sup>a</sup>
Phenothiazine	513, 439	515, 437 <sup>a</sup>
Tetrathiofulvalene	578, 434	580, 435 <sup>a</sup>
Biphenyl	657	660 <sup>e</sup>
Tetraphenyl ethylene	495	495 <sup>f</sup>
Tris <i>p</i> -bromo phenyl amine	726	725 <sup>a</sup>
Tetramethyl- <i>p</i> -phenylene diamine	615, 565	618, 567 <sup>a</sup>
Ferrocene	619.5	619 <sup>a</sup>
1,4-Dimethoxybenzene	472, 437	475, 440 <sup>g</sup>

*a*, for references see Handoo *et al*<sup>6</sup>; *b*, not located in literature; *c*, reported in ref. 4; *d*, ref. 12; *e*, ref. 13; *f*, ref. 14; *g*, ref. 15.

(ii) It was found that when DDQ is replaced by PbO<sub>2</sub>, MnO<sub>2</sub> or even the weak oxidant, *p*-nitrobenzenediazonium tetrafluoroborate or dibenzoyl peroxide, in which the possibility of protonation does not arise, an identical sequence of reactions occurs in TFA/CH<sub>2</sub>Cl<sub>2</sub> solution and the cation radicals of all the compounds listed in table 1 are formed.

Thus, whether the oxidant is DDQ or PbO<sub>2</sub>, we believe that the requisite single electron transfers are accomplished as summarized in equation (2)



It is pertinent to mention here that the activation of metal oxidants in TFA and other strong acids has been



observed with Co(IV), Pb(IV), Mn(III), Ce(IV), Cu(II) etc<sup>11</sup>. It would, therefore, be of interest and possibly profitable to speculate upon the emergence of a host of reagents as strong one-electron oxidants in the said solvent system. Work in this direction is in progress.

1 April 1986

1. Foster, R., In: *Organic charge transfer complexes*, Academic Press, London, 1969.
2. Foster, R. and Hanson, P., *Biochim. Biophys. Acta*, 1961, **47**, 596.
3. Beresford, P., Ales, D. H., Krika, L. J. and Ledwith, A., *J. Chem. Soc. Perkin Trans. 1*, 1974, 276.
4. Sep, W. J., Verhoeven, J. W. and DeBoer Th. J., *Tetrahedron*, 1979, **35**, 2161.
5. Ebersson, L., *Adv. Phys. Org. Chem.*, 1982, **18**, 79.
6. Handoo, K. L., Handoo, S.K., Gadru, K. and Kaul, A., *Tetrahedron Lett.*, 1985, **26**, 1765.
7. Paul, M. A. and Long, F. A., *Chem. Rev.*, 1957, **57**, 1.
8. Nepras, M., Kratochvil, V., Titz, M., Novak, A. and Slavik, V., *Coll. Czech. Chem. Commun.*, 1973, **38**, 1003.
9. (a) Norman, R. O. C., Thomas, C. B. and Willson, J. S., *J. Chem. Soc. B*, 1971, 518; (b) Partch, R. E., *J. Am. Chem. Soc.*, 1967, **89**, 3662; (c) Kochi, J. K., Tang, R. T. and Bernath, T., *J. Am. Chem. Soc.*, 1973, **95**, 7114.
10. Bard, A. J., Ledwith, A. and Shine, H. J., *Adv. Phys. Org. Chem.*, 1976, **13**, 155.
11. (a) Heiba, E. I., Dessau, R. M. and Koehl, Jr. W. J., *J. Am. Chem. Soc.*, 1969, **91**, 138, 6830; (b) Heiba, E. I. and Dessau, R. M., *J. Am. Chem. Soc.*, 1971, **93**, 995.
12. Das, M. and Basu, S., *Spectrochim. Acta*, 1961, **17**, 897.
13. Sehested, K. and Hart, H. J., *J. Phys. Chem.*, 1975, **79**, 1639.
14. Shida, T. and Hamill, W. H., *J. Chem. Phys.*, 1966, **44**, 2375.
15. Zarubin, M. Ya., Kutnevich, A. M. and Rudenko, A. P., *Zh. Org. Khim.*, 1975, **11**, 1284.

## POLYMER SUPPORTED PERIODATE: CONVENIENT METHOD FOR OXIDATION OF HYDRAZIDES

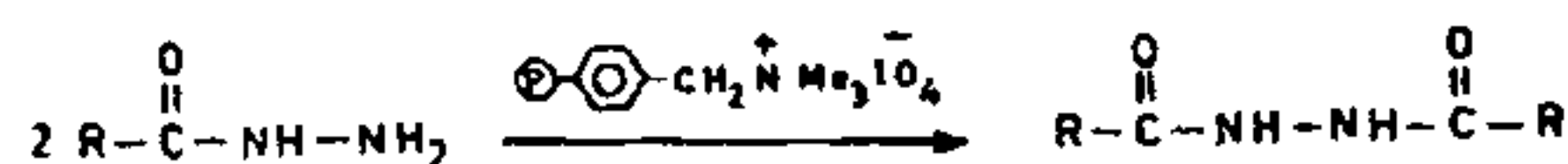
D. G. SALUNKHE, M. H. JAGDALE,  
S. S. SWAMI and M. M. SALUNKHE\*

*Department of Chemistry, Shivaji University,  
Kolhapur 416 004, India.*

EARLIER work on the oxidation of the hydrazides reveals that they can be oxidized to 1,2 diacyl hydrazines with diphenyl selenoxide<sup>1</sup>, benzene selenic acid<sup>2</sup> and with aryl sulphonyl peroxides<sup>3</sup>. However, in all these methods reported, the side products which were formed result in low yields of 1,2 diacyl hydrazines.

Recently Hodge<sup>4</sup> reported polymer-supported periodate as a good oxidizing agent in the range of solvents and oxidized various quinols, catechols, glycols, triphenyl phosphine, hydrazobenzene and benzohydroxamic acid.

In continuation of our work on polymer-supported reactions<sup>5,6</sup> we now report the oxidation of hydrazides with polymer-supported periodate to 1,2 diacyl hydrazines in high yields and purity. The products of the reaction with polymer-supported periodate were isolated simply by filtering off the resin and evaporating the solvent from the filtrate. Thus the method has advantage in terms of yields and simplicity of the performance.



Interestingly this method is inexpensive as the resin could be used repeatedly since it can be regenerated to its initial activity by treatment with dilute hydrochloric acid.

All melting points were taken in open capillaries and were uncorrected. The purity of the compound was checked on silica gel TLC plates using iodine vapours as developer. IR and NMR spectra were recorded on Perkin Elmer spectrometer. NMR spectra were taken in DMSO-D6 using TMS as internal reference.

*Polymer-supported periodate:* The chloride form of Amberlyst A26 (25 g damp) was stirred for 6 hr with sodium periodate (20 g) in water at 20°C. The liquid was decanted off and the resin was treated with a fresh solution of sodium periodate (20 g) in water (200 ml). The resin was then filtered off and washed successively with water (4 × 200 ml), tetrahydrofuran (2 × 100 ml)