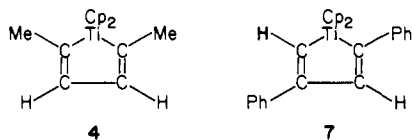


Figure 1. Configurations of $\text{Cp}_2\text{Ti}(\text{C}_2\text{H}_2)\text{PMe}_3$ and $\text{Cp}_2\text{Ta}(\text{C}_2\text{H}_4)\text{H}$.

firmly the carbon hydrogen ratio of 1:1. The polymerization turnover rate under 1 bar of C_2H_2 pressure is approximately 120. The compressed polymer exhibits a characteristic metallic luster and shows a singlet signal in the EPR spectrum. It absorbs oxygen readily from the air up to 25% by weight and can be doped with iodine.

The reactivity of **1** with substituted alkynes has also been investigated. The reaction of methylacetylene and **1** followed by pentane extraction of the residue afforded the metallacycle $\text{Cp}_2\text{TiC}_4\text{Me}_2\text{H}_2$ (**4**).¹¹ This structural assignment is based upon ^1H and ^{13}C NMR data. Preliminary ^1H and ^{13}C NMR spectral data indicate that the other two possible isomers of **4** are also produced. Dimethylacetylene and **1** give the metallacycle $\text{Cp}_2\text{TiC}_4\text{Me}_4$ (**5**)¹² as the main product. Phenylacetylene and **1** form the alkyne complex $\text{Cp}_2\text{Ti}(\text{PhC}_2\text{H})\text{PMe}_3$ (**6**)¹³ and the metallacycle $\text{Cp}_2\text{TiC}_4\text{Ph}_2\text{H}_2$ (**7**).¹⁴ Diphenylacetylene and **1** react



in an analogous manner producing $\text{Cp}_2\text{Ti}(\text{C}_2\text{Ph}_2)\text{PMe}_3$ ¹⁵ and $\text{Cp}_2\text{TiC}_4\text{Ph}_4$.¹⁶

Further investigations concerning the reactivity of **2** and **3** as well as other alkyne derivatives of group 4 metals are in progress.

Acknowledgment. This research has been supported in part by a National Science Foundation-Deutsche Forschungsgemeinschaft International Cooperation Grant (NSF INT-8111979) to M.D.R. and H.G.A., in connection with the U.S.-Germany Cooperative Science Program, as well as by NSF and DFG research grants to M.D.R. and H.G.A., respectively. H.G.A. also thanks the Fonds der Chemischen Industrie for financial support; M.D.R. is grateful to the Alexander von Humboldt Stiftung for a Senior U.S. Scientist Award.

(10) **3**: Anal. Calcd for $(\text{CH})_2$: C, 92.26; H, 7.74. Found: C, 90.38; H, 7.59; Ti, 0.90.

(11) **4**: ^1H NMR (CDCl_3) δ 6.10 (10 H), 5.37 (2 H), 1.60 (6 H); ^{13}C NMR (CDCl_3) δ 201.5 (C_α), 115.2 (C_β), 112.0 (Cp), 27.1 (Me); MS, m/z 258 (M^+); IR $\nu(\text{C}=\text{C})$ 1440 cm^{-1} (KBr).

(12) **5**: ^1H NMR (CDCl_3) δ 5.95 (10 H), 1.28 (6 H), 1.13 (6 H); ^{13}C NMR (CDCl_3) δ 192.1 (C_α), 122.3 (C_β), 111.7 (Cp), 19.1, 14.0 (Me); MS, m/z 286 (M^+); IR $\nu(\text{C}=\text{C})$ 1438 cm^{-1} (KBr).

(13) **6**: ^1H NMR (toluene- d_6) δ 7.13 (m, 5 H), 5.83 (br, 10 H), 0.93 (d, 5.4 Hz, 9 H); ^{31}P NMR δ 26.8; MS, m/z 354 [(M-2H) $^+$]; IR $\nu(\text{C}=\text{C})$ 1590 cm^{-1} (KBr).

(14) **7**: ^1H NMR (CDCl_3) δ 7.23 (m, 10 H), 6.24 (10 H); ^{13}C NMR (CDCl_3) δ 198.6 (PhC_α), 196.7 (HC_α) [$^1J(\text{C},\text{H}) = 140.7$, $^3J(\text{C},\text{H}) = 10.3$ Hz], 147.0, 141.2, 127.9, 125.1 (Ph), 146.6, 141.2, 127.7, 124.7 (Ph), 130.1 (PhC_β), 128.7 (HC_β); MS, m/z 386 (M^+).

(15) Demerseman, B.; Dixneuf, P. H. *J. Chem. Soc., Chem. Commun.* **1981**, 665.

(16) (a) Alt, H.; Rausch, M. D. *J. Am. Chem. Soc.* **1974**, *96*, 5936. (b) Rausch, M. D.; Boon, W. H.; Alt, H. G. *J. Organomet. Chem.* **1977**, *141*, 299. (c) Atwood, J. L.; Hunter, W. E.; Alt, H.; Rausch, M. D. *J. Am. Chem. Soc.* **1976**, *98*, 2454.

Threshold Resonances in Electron Photodetachment Spectra. Structural Evidence for Dipole-Supported States

Jeffrey Marks, Paul B. Comita, and John I. Brauman*

Department of Chemistry, Stanford University
Stanford, California 94305

Received December 27, 1984

The existence of a bound state arising from the interaction of a neutral dipole and an electron was first predicted by Fermi and Teller in 1947.¹ They calculated that for a nonrotating point dipole a critical value of 1.625 D is necessary for a bound state to exist. Additional calculations have examined the influence of finite-length and rotating dipole moments on the critical value.² In this paper we provide structural evidence for such "dipole-supported" states arising from the interaction of a dipolar molecule and an electron.

Experimental evidence for the existence of dipole-supported states is limited. Electron scattering experiments on polar molecules have been carried out and have been interpreted as involving such states.³ It has recently been proposed that resonances observed in the threshold region for electron photodetachment from molecular negative ions correspond to transitions to dipole-supported states.⁴ Resonances have been observed in the electron photodetachment spectra of enolate anions indicating the presence of an electronically excited state occurring at the threshold for electron photodetachment.⁵ Quantum mechanical calculations have been carried out for acetaldehyde enolate and have indicated the presence of a low-lying, non-valence electronic state near the photodetachment threshold.⁶ The assignment of these resonances to dipole-supported states is strengthened considerably by recent very high resolution (0.0007 cm^{-1}) electron photodetachment experiments on acetaldehyde.⁷ These experiments show that in the excited state the higher rotational states are not bound and that the excited-state geometry is very similar to that of the neutral radical.

We report here a further test of this model, in which photodetachment cross sections were measured for a pair of ions for which the neutral dipolar core could be varied without substantially changing the electronic structure of the anions. In this experiment, resonances at the threshold of electron photodetachment due to dipole-bound electronic states should be present only for the anion with a critical dipole moment.

One such set of molecules is *o*- and *p*-benzoquinone (OBQ and PBQ, respectively, structures in Figure 1). The symmetrical PBQ has no dipole moment; the dipole moment of OBQ is approximately⁸ 5.1 D. Both of these neutral molecules have positive electron affinities and both form stable negative ions. The negative ions have similar electronic structures,⁹ and we would expect that the large dipole moment of OBQ should support a quasi-bound electronically excited state, while that of PBQ would not. An excited electronic state above the threshold energy will give rise to a resonance in the spectrum corresponding to an additional channel opening besides direct photodetachment.¹⁰

(1) Fermi, E.; Teller, E. *Phys. Rev.* **1947**, *72*, 406.

(2) Garrett, W. R. *Chem. Phys. Lett.* **1970**, *5*, 393. Garrett, W. R. *Phys. Rev. A* **1971**, *3*, 961. Also see: Jordan, K. D. *Acc. Chem. Res.* **1979**, *12*, 36.

(3) Wong, S. F.; Schulz, G. J. *Phys. Rev. Lett.* **1974**, *33*, 134. Rohr, K.; Linder, F. J. *Phys. B* **1976**, *9*, 2521.

(4) Zimmerman, A. H.; Brauman, J. I. *J. Chem. Phys.* **1978**, *66*, 5823. Jackson, R. L.; Zimmerman, A. H.; Brauman, J. I. *J. Chem. Phys.* **1979**, *71*, 2088.

(5) Jackson, R. L.; Hiberty, P. C.; Brauman, J. I. *J. Chem. Phys.* **1981**, *74*, 3705.

(6) Wetmore, R. W.; Schaefer, H. F.; Hiberty, P. C.; Brauman, J. I. *J. Am. Chem. Soc.* **1980**, *102*, 5470.

(7) Lykke, K. R.; Mead, R. D.; Lineberger, W. C. *Phys. Rev. Lett.* **1984**, *52*, 2221. Mead, R. D.; Lykke, K. R.; Lineberger, W. C.; Marks, J.; Brauman, J. I. *J. Chem. Phys.* **1984**, *81*, 4883.

(8) Nagakura, S.; Kuboyama, A. *J. Am. Chem. Soc.* **1954**, *76*, 1003.

(9) Electron affinities were assigned by analysis of the threshold behavior of the photodetachment cross sections.¹²

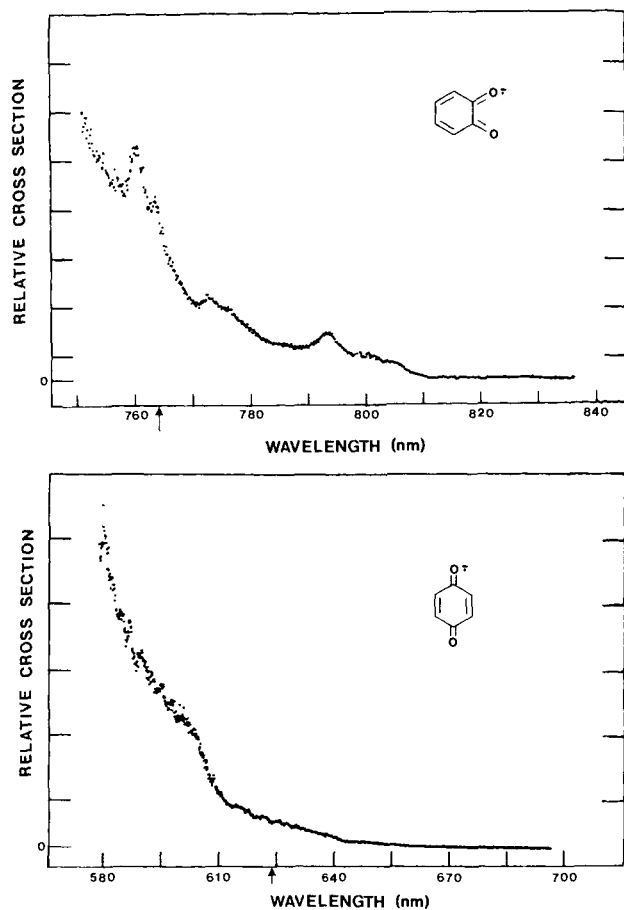


Figure 1. Electron photodetachment spectra of *o*-benzoquinone (upper) and *p*-benzoquinone (lower) obtained with a 1-cm⁻¹ resolution. The arrows indicate threshold assignments for adiabatic electron affinities.

To determine if any threshold states exist in these anions we recorded the electron photodetachment spectrum of the two radical anions. These experiments were carried out in an ion cyclotron resonance spectrometer, using a Coherent 590 dye laser with a 1-cm⁻¹ line width as a light source. Details of the experimental apparatus have been reported.^{4,11} The anion of PBQ was generated from electron capture by PBQ and the anion of OBQ was formed by dissociative electron impact on the cyclic sulfite of catechol. In Figure 1 we present the laser photodetachment spectra of OBQ⁻ and PBQ⁻. The adiabatic electron affinities were assigned to threshold values of approximately 1.99 and 1.62 eV for PBQ and OBQ, respectively.¹²

Several resonances appear in the photodetachment spectrum of OBQ, the most intense of which are at 793, 764, and 761 nm. The threshold assignment for the adiabatic electron affinity of OBQ is at 764 nm, the position of one of the sharp resonances. A Fano line-shape analysis using the location of the resonance with respect to the continuum threshold as an adjustable parameter⁴ places the threshold assignment at the position of the resonance corresponding to the 0-0 vibronic transition. The 0-0 transition has been found to occur at the assigned threshold energy for many structurally different enolate anions.^{4,5} The small relative cross section for photodetachment at energies below the assigned threshold suggests photodetachment from vibrationally excited anion states (hot bands). The resonances lower in energy than the threshold are presumably due to hot band transitions to the dipole-supported state.

(10) Drzaic, P. S.; Marks, J.; Brauman, J. I. In "Gas Phase Ion Chemistry"; Bowers, M. J., Ed.; Academic Press: New York, 1984; Vol. 3, p 167. Mead, R. D.; Stevens, A. E.; Lineberger, W. C. *Ibid.* p 214.

(11) Details of the modification of the experimental apparatus will be reported in a future manuscript.

(12) Comita, P. B.; Marks, J.; McPeters, H. L.; Brauman, J. I., manuscript in preparation.

The two threshold resonances are separated by 55 cm⁻¹ and may be due to different vibrational modes or possibly different rotational branches of one vibration. The width of the resonances is about 45 cm⁻¹ and is governed by a manifold of rotational transitions. The hot band resonance at 793 nm is separated from the threshold resonances by 541 and 486 cm⁻¹, corresponding to a low-frequency vibrational mode.

No fine structure at threshold was observed in the spectrum of the PBQ anion. Broad resonances due to valence excited states appear at much shorter wavelengths than the threshold region shown here. Similar valence excited-state resonances appear at shorter wavelengths in the OBQ⁻ spectrum, verifying that the valence excited states in these anions are very similar.¹² The observation of threshold resonances occurring only for the dipolar molecule is consistent with the picture that a large dipole is required for a quasi-bound state to exist.

Acknowledgment. This work was supported by the National Science Foundation and the donors of the Petroleum Research Fund, administered by the American Chemical Society. We thank the Exxon Education Foundation for fellowship support for J.M.

Registry No. OBQ radical anion, 20526-43-6; PBQ radical anion, 3225-29-4.

Dependence of Rate Constants of Heterogeneous Electron Transfer Reactions on Viscosity

X. Zhang, Johna Leddy, and Allen J. Bard*

Department of Chemistry
The University of Texas at Austin
Austin, Texas 78712

Received March 6, 1985

Studies presented here of the electrochemical behavior of the Fc(CN)₆^{3-/4-} couple in aqueous and the Fc^{0/+} couple (Fc is ferrocene) in dimethyl sulfoxide (Me₂SO) solutions of different viscosities demonstrate that even for reactions that are far from the diffusion-controlled limit, the heterogeneous electron transfer (et) rate constant, *k*⁰, strongly depends upon viscosity. The effect of the solvent on rate constants of et reactions has been considered in a number of papers,¹⁻⁴ although explicit experimental studies of the effect of solvent viscosity on heterogeneous or homogeneous et are uncommon. Our interest in this topic was initiated during studies of the et kinetics at polymer-modified electrodes.⁵ The rate constants for the reactants bound in polymer layers on an electrode surface were 2-3 orders of magnitude smaller than those for the same reactants dissolved in solution. The diffusion processes were also generally 10² to 10⁵ times slower in the polymer matrix than in solution.⁵ This apparent correlation between the observed rate constant, *k*⁰, and the diffusion coefficient, *D*, for reactants confined in polymer films is also evident in other studies of polymer-modified electrodes.⁶ To assure that these reactions were far from the diffusion-controlled limit (where a dependence of *k*_{obs} on *D* is clearly expected) and to make comparisons in less complicated media, we studied two different electrode reactions in solutions in which viscosities were varied by additives thought to have a minor effect on other variables (e.g., dielectric constant or electrode surface properties).

(1) (a) Calef, D. F.; Wolynes, P. G. *J. Phys. Chem.* **1983**, *87*, 3387. (b) *J. Chem. Phys.* **1983**, *78*, 470. (c) Frauenfelder, H.; Wolynes, P. G. *Science (Washington, D.C.)*, in press.

(2) (a) Hupp, J. T.; Weaver, T.; Weaver, M. J. *J. Electroanal. Chem.* **1983**, *152*, 1. (b) Weaver, M. J.; Gennett, T. *Chem. Phys. Lett.* **1985**, *113*, 213. (c) Gennett, T.; Milner, D. F.; Weaver, M. J. *J. Phys. Chem.*, submitted for publication.

(3) Kapturkiewicz, A.; Behr, B. *J. Electroanal. Chem.* **1984**, *179*, 187.

(4) Aleksandrov, I. V.; Gol'danskii, V. I. *J. Chem. Phys.* **1984**, *87*, 455.

(5) (a) Leddy, J.; Bard, A. J. *J. Electroanal. Chem.*, in press. (b) White, H.; Leddy, J.; Bard, A. J. *J. Am. Chem. Soc.* **1982**, *104*, 4811. (c) Krishnan, M.; Zhang, X.; Bard, A. J. *J. Am. Chem. Soc.* **1984**, *106*, 7371.

(6) Oyama, W.; Ohsaka, T.; Ushirogouchi, T. *J. Phys. Chem.* **1984**, *88*, 5274. (b) Oyama, N.; Ohsaka, T. *J. Am. Chem. Soc.* **1983**, *105*, 6003.