J. Am. Chem. Soc. 1993, 115, 201-204

Determination of the Kinetic Parameters for the Electroreduction of C_{60} by Scanning Electrochemical Microscopy and Fast Scan Cyclic Voltammetry

Michael V. Mirkin, Luis O. S. Bulhões,[†] and Allen J. Bard*

Contribution from the Department of Chemistry and Biochemistry, The University of Texas at Austin, Austin, Texas 78712. *Received August 11, 1992*

Abstract: The electroreduction of the fullerene C_{60} in 1,2-dichlorobenzene (ODCB) and benzonitrile (PhCN) at a Pt electrode was studied by using scanning electrochemical microscopy and fast scan cyclic voltammetry. The former technique was employed for steady-state measurements in a thin-layer cell formed by an ultramicroelectrode tip and mercury pool substrate. The standard heterogeneous rate constants found in both solvents, 0.46 cm/s (ODCB) and 0.12 cm/s (PhCN), appeared to be lower than one would expect for an uncomplicated outer sphere electron-transfer reaction, probably because solvation and ion pairing affect the reaction kinetics. The diffusion coefficient of C_{60} in ODCB depends strongly on supporting electrolyte ($TBABF_4$) concentration.

Introduction

The electrochemistry of C_{60} in different solvents has been the subject of several studies.[1-7] Voltammetric parameters (e.g., half-wave potentials relative to the Fc^+/Fc couple) have been reported for up to six[3,4] reversible steps in the electroreduction of C_{60}, and the effects of solvent, supporting electrolyte, and temperature have been discussed.[1c,3] We report here a study of the rate of heterogeneous electron transfer (ET) to C_{60} to form the monoanion. Fawcett et al.[6] recently measured the heterogeneous ET rate constant in PhCN by an alternating current method at a microdisk electrode (radius of 25 μm). We have recently developed a steady-state method for the measurements of very rapid ET reaction rates in a very thin layer of solution trapped between an ultramicroelectrode (UME) and a mercury pool.[8] This technique has the advantage of being relatively free from artifacts arising from uncompensated resistance, which can be particularly troublesome in the highly resistive solvents in which C_{60} is soluble. We used this approach in our study of C_{60} reduction and compare this method to fast scan cyclic voltammetry (CV) at an UME. One would expect the heterogeneous ET rate constant k^0 to be large, since the k^0s for the reduction of aromatic hydrocarbons such as anthracene in solvents like *N,N*-dimethylformamide (DMF) are large (>1 cm/s). This is usually ascribed to the small reorganization energies associated with the formation of large anions.[9] We describe here the determination of kinetic parameters and diffusion coefficients for the first stage of reduction of C_{60} in two solvents, 1,2-dichlorobenzene (ODCB) and benzonitrile (PhCN).

Experimental Section

C_{60} was separated from a carbonaceous soot (Texas Fullerenes Inc., Houston, TX) as previously described.[10] The concentrations of the C_{60} solutions were determined spectrophotometrically[10] from spectra in the region of 400–405 nm. The calibration curve was obtained using the sharp peak at 404 nm ($\epsilon_{max} = 124$) from solutions prepared from samples of C_{60} dried in a vacuum oven at 200 °C for 24 h (to remove any residual solvent from the purification stage). Solutions were deoxygenated with purified argon before each experiment. Triply-distilled mercury (Bethlehem Apparatus Co., Hellertown, PA) was treated with oxygen-saturated nitric acid for 24 h and filtered before use. Benzonitrile and 1,2-dichlorobenzene (Aldrich Chemical Co., Milwaukee, WI) were used as received. Tetra-*n*-butylammonium tetrafluoroborate ($TBABF_4$, Southwestern Analytical Chemicals, Inc., Austin TX) was recrystallized twice from ethyl acetate/ether (9:1) and dried under vacuum at 120 °C for 72 h. Ferrocene (Fluka Chemical Corp., Ronkonkoma, NY) was sublimed twice before use.

Carbon (5.5-μm radius) and platinum (from 1- to 12.5-μm radius) microdisk tip electrodes were fabricated as described[11] and polished with 0.05-μm alumina before measurements. A Pt foil counter electrode and a Ag wire quasireference electrode were used in the voltammetric experiments.

The scanning electrochemical microscopy (SECM) apparatus was described previously,[12] as were the operational procedures for the SECM with a mercury pool substrate.[8] As discussed, SECM-controlled movement of the tip into the Hg pool under vibration-free conditions reproducibly trapped thin layers of solution, the dimensions of which can be determined from the thin-layer cell (TLC) limiting current, as shown below. The SECM/TLC measurements were performed in a two-electrode mode. The cyclic voltammograms were obtained using an E1–400 four-electrode potentiostat (Ensman Instruments, Bloomington, IN), a BAS-100A electrochemical analyzer (Bioanalytical Systems, West Lafayette, IN), or a PAR 173 potentiostat with a Model 175 programmer (EG&G Princeton Applied Research, Princeton, NJ).

The ferrocenium/ferrocene (Fc^+/Fc) couple was used as an internal standard for potential referencing and ohmic drop compensation in fast scan experiments. The appropriate concentration of ferrocene was chosen to produce peak currents for both C_{60}/C_{60}^- and Fc^+/Fc redox reactions that were approximately equal. This allows for proper adjustment of the *iR*-drop compensation by making the peak separation (ΔE_p) for the Fc^+/Fc couple 59–60 mV, since this reaction is essentially nernstian in our experiments, thus ensuring the proper compensation for C_{60}/C_{60}^- as well.

Results and Discussion

Cyclic Voltammetry. The steady-state voltammograms at a well-characterized carbon microdisk electrode (5.5-μm radius, as confirmed by optical microscopy and independent electrochemical measurements[8]) were employed to determine the diffusion coefficient (D) of C_{60} in both solvents. Values of 3.88×10^{-6} and 3.14

---

[1] (a) Dubois, D.; Kadish, K. M.; Flanagan, S.; Haufler, R. E.; Chibante, L. P. F.; Wilson, L. J. *J. Am. Chem. Soc.* **1991**, *113*, 4364. (b) Dubois, D.; Kadish, K. M.; Flanagan, S.; Wilson, L. J. *J. Am. Chem. Soc.* **1991**, *113*, 7773. (c) Dubois, D.; Moninot, G.; Kutner, W.; Jones, M. T.; Kadish, K. M. *J. Phys. Chem.* **1992**, *96*, 7137.

[2] (a) Allemand, P.-M.; Koch, A.; Wudl, F.; Rubin, Y.; Diederich, F.; Alvarez, M. M.; Anz, S. J.; Whetten, R. L. *J. Am. Chem. Soc.* **1991**, *113*, 1050.

[3] Xie, Q.; Perez-Cordero, E.; Echegoyen, L. *J. Am. Chem. Soc.* **1992**, *114*, 3978.

[4] Ohsawa, T.; Saji, T. *J. Chem. Soc., Chem. Commun.* **1992**, 281.

[5] (a) Jehoulet, C.; Obeng, Y. S.; Kim, Y.-T.; Zhou, F.; Bard, A. J. *J. Am. Chem. Soc.* **1992**, *114*, 4237. (b) Jehoulet, C.; Bard, A. J.; Wudl, F. *J. Am. Chem. Soc.* **1991**, *113*, 5456.

[6] Fawcett, W. R.; Opallo, M.; Fedurco, M.; Lee, J. W. *J. Am. Chem. Soc.*, preceding article in this issue.

[7] Miller, B.; Rosamilia, J. M.; Dabbagh, G.; Muller, A. J.; Haddon, R. C. *J. Electrochem. Soc.* **1992**, *139*, 1941.

[8] Mirkin, M. V.; Bard, A. J. *J. Electrochem. Soc.* **1992**, *139*, 3535.

[9] Kojima, H.; Bard, A. J. *J. Am. Chem. Soc.* **1975**, *97*, 6317.

[10] (a) Hare, J. P.; Kroto, H. W.; Tayler, R. *Chem. Phys. Lett.* **1991**, *177*, 394. (b) Ajie, H.; Alvarez, M. M.; Anz, S. J.; Beck, R. D.; Diederich, F.; Fostiropoulos, K.; Huffman, D. R.; Kratschmer, W.; Rubin, Y.; Schriver, K. E.; Sensharma, D.; Whetten, R. L. *J. Phys. Chem.* **1990**, *94*, 8630.

[11] Bard, A. J.; Fan, F.-R. F.; Kwak, J.; Lev, O. *Anal. Chem.* **1989**, *61*, 1794.

[12] Wipf, D. O.; Bard, A. J. *J. Electrochem. Soc.* **1991**, *138*, 496.

[†] Permanent address: Departamento de Química, Universidade Federal de São Carlos, São Carlos, SP, Brazil.

0002-7863/93/1515-201$04.00/0

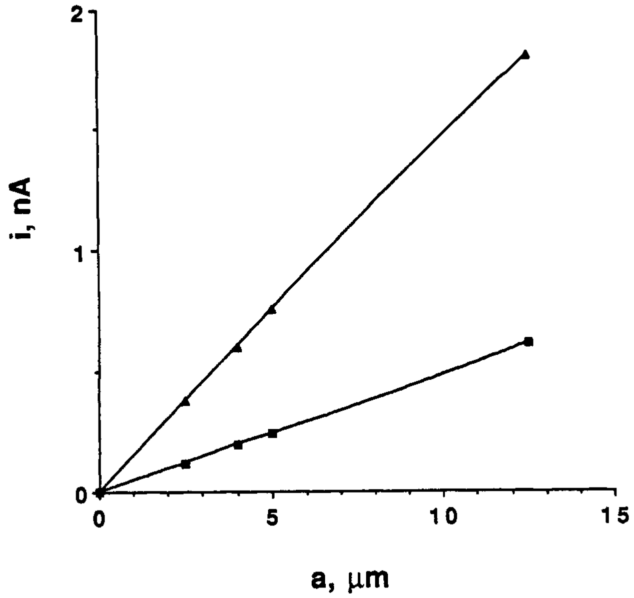

Figure 1. Steady-state diffusion-limited current as a function of the microdisk radius. (■) 0.4 mM C_{60} in PhCN with 0.05 M $TBABF_4$. (▲) 1.0 mM C_{60} in ODCB with 0.1 M $TBABF_4$.

$\times 10^{-6}$ cm^2/s were found for ODCB (with 0.1 M $TBABF_4$) and PhCN (with 0.05 M $TBABF_4$), respectively, from the microdisk diffusion-limited current expressed as

$$i_{t,\infty} = 4nFDc^*a \tag{1}$$

where n is the number of electrons involved in the electrode reaction, F is the Faraday constant, c^* is the bulk concentration of the electroactive species, and a is the disk radius. These values of D are in agreement with those obtained from steady-state voltammograms at different size microelectrodes and different concentrations of C_{60} (Figure 1). Numerous previous experiments in our laboratory and elsewhere[13] have shown the validity of such microelectrode determinations of D. The straight lines in Figure 1 yield D values of 3.9×10^{-6} (ODCB) and 3.2×10^{-6} cm^2/s (PhCN). While these diffusion coefficients are much larger than those reported previously,[1c,7] the discrepancies are caused by differences in the supporting electrolyte concentration (e.g., 0.5 M TBABr in ref 7 vs 0.1 M $TBABF_4$ here). Indeed, we found that the diffusion coefficient of C_{60} is surprisingly dependent on electrolyte concentration, so the limiting current at the microdisk decreased strongly for a 1.32 mM solution of C_{60} in ODCB as the $TBABF_4$ concentration increased: $i_{t,\infty}$ = 1.5, 0.55, and 0.49 nA for $TBABF_4$ concentrations of 0.1, 0.3, and 0.5 M, respectively. Moreover, in previous papers the concentration was obtained directly from the weight of C_{60} employed rather than determined by spectrophotometry of the solution. Residual solvent, which is difficult to remove completely, remaining on the C_{60} sample following purification could lead to the overestimation of the C_{60} concentration and underestimation of D.

The steady-state voltammograms obtained at a carbon microdisk were analyzed using the approach previously described.[14,15] The quartile potentials ($E_{1/4}$, $E_{1/2}$, and $E_{3/4}$) were determined from the digitized data, and their differences $\Delta E_{1/4} = E_{1/4} - E_{1/2}$ and $\Delta E_{3/4} = E_{1/2} - E_{3/4}$ were about 29 mV for both solvents, i.e., these voltammograms were essentially Nernstian.[14]

Using the above D values and eq 1, we estimated the effective radius for a small platinum tip (nominally 1 µm) whose shape, unlike larger electrodes, deviated from the perfect disk shape. Values for a of 1.05 and 1.1 µm were found in ODCB and PhCN, respectively. The small difference in the two solvents might be caused by a slight change in the surface area of the small electrode with polishing. The difference between the quartile potentials found from steady-state voltammograms at this Pt microdisk (Figure 2) are $\Delta E_{1/4} = 31 \pm 0.5$ mV and $\Delta E_{3/4} = 35.5 \pm 0.5$ mV (ODCB, curve 1); $\Delta E_{1/4} = 31.5 \pm 1$ mV and $\Delta E_{3/4} = 33.5 \pm 1.5$ mV (PhCN, curve 2). The higher uncertainties in the latter data are caused by the lower concentration of C_{60} in PhCN, which resulted in a quite low diffusion current (about 50 pA) and greater interferences of noise and background current. According to Table II in ref 14, both of these sets of data allow only bracketing rather than quantitative determination of the kinetic parameter values (i.e., the dimensionless parameter $\lambda = ak^0/d$, the standard rate constant k^0, and the transfer coefficient α): $1 \leq \lambda \leq 20$, 0.1 cm/s $\leq k^0 \leq 1$ cm/s, and $0.3 \leq \alpha \leq 0.7$. Thus, a faster electrochemical method is required to obtain more reliable values of the kinetic parameters.

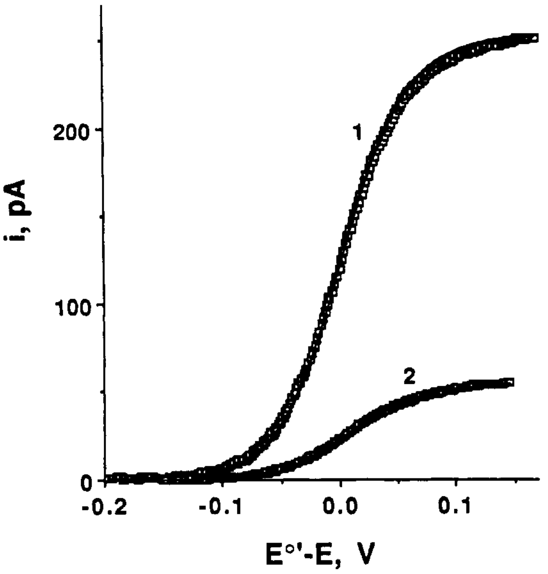

Figure 2. Steady-state voltammograms of the first reduction of C_{60} in (1) ODCB with 0.1 M $TBABF_4$ supporting electrolyte and (2) PhCN with 0.05 M $TBABF_4$ at a 1-µm-radius Pt microdisk. c^* = 1.6 mM (1) and 0.38 mM (2). v = 10 mV/s. Squares represent experimental data, and the solid lines are theoretical curves calculated by using eq 13 from ref 15 and the kinetic parameters given in the text.

In agreement with previous reports,[1,3] CV obtained in both solvents at a moderate scan rate (e.g., v = 1 V/s) showed four pairs of reversible one-electron voltammetric peaks, with ΔE_p of about 60 mV, independent of v, in the potential range between 0 and −2.0 V vs Fc^+/Fc. In this study we focused our attention on the first wave. This wave is less sensitive to oxygen than the subsequent ones, which was a consideration in our SECM experiments, where rigorous removal of oxygen is difficult. At scan rates higher than 2 V/s, the increase in peak separation is caused mostly by uncompensated potential drop in these highly resistive solutions. Using the approach described in the Experimental Section, we were able to compensate the iR-drop for Fc^+/Fc for the scan rate in the range from 5 to 50 V/s. Under conditions where ΔE_p for Fc^+/Fc was 60 mV, cyclic voltammograms at v = 20 V/s showed ΔE_p of about 63 (PhCN) and 61 mV (ODCB) (Figure 3). However, because of uncertainties in digital sampling (about 0.5–1 mV in these experiments), imperfect iR compensation, and interference of charging current (which is most significant in PhCN, where the low solubility did not allow the concentration of C_{60} to be higher than about 0.4 mM) errors in the determined ΔE_p values can be as large as ±2–3 mV. Thus, again, we can only set lower limits for the rate constants:[16] 0.5 cm/s $\leq k^0$(ODCB) and 0.2 cm/s $\leq k^0$(PhCN).

SECM/TLC Measurements. We have demonstrated previously[8,17] the possibility of achieving higher rates of mass transport

---

(13) (a) Wightman, R. M.; Wipf, D. O. *In Electroanalytical Chemistry*; Bard, A. J., Ed.; Marcel Dekker: New York, 1989; Vol. 15, p 267. (b) See, e.g., Denuault, G.; Mirkin, M. V.; Bard, A. J. *J. Electroanal. Chem.* **1991**, *308*, 27.

(14) Mirkin, M. V.; Bard, A. J. *Anal. Chem.* **1992**, *64*, 2293.

(15) Oldham, K. B.; Zoski, C. G. *J. Electroanal. Chem.* **1988**, *256*, 11.

(16) Nicholson, R. S. *Anal. Chem.* **1965**, *37*, 1351.

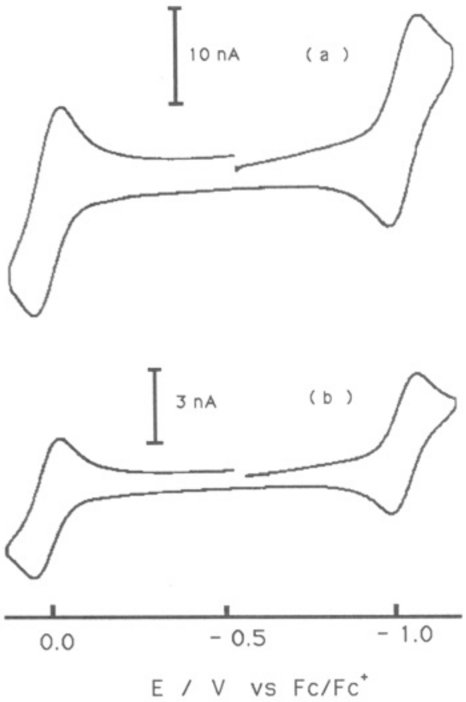

Figure 3. Cyclic voltammograms of C_{60}, with *iR*-drop compensation with a Fc^+/Fc internal standard at a 12.5-μm-radius Pt microdisk. (a) 1.5 mM C_{60} in ODCB with 0.1 M $TBABF_4$ and 0.6 mM Fc. (b) 0.4 mM C_{60} in PhCN with 0.05 M $TBABF_4$ and 0.3 mM of Fc. v = 20 V/s.

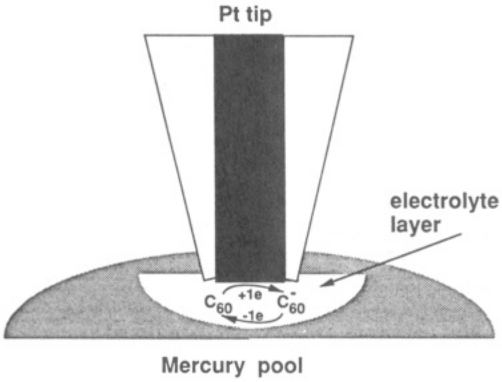

Figure 4. Schematic representation of the TLC formed inside the Hg pool. C_{60} is reduced at the Pt tip surface to produce C_{60}^-, which is reoxidized at the Hg anode. The solution layer is shown greatly enlarged for clarity; the actual solution layer thickness l is smaller than the electrode radius a.

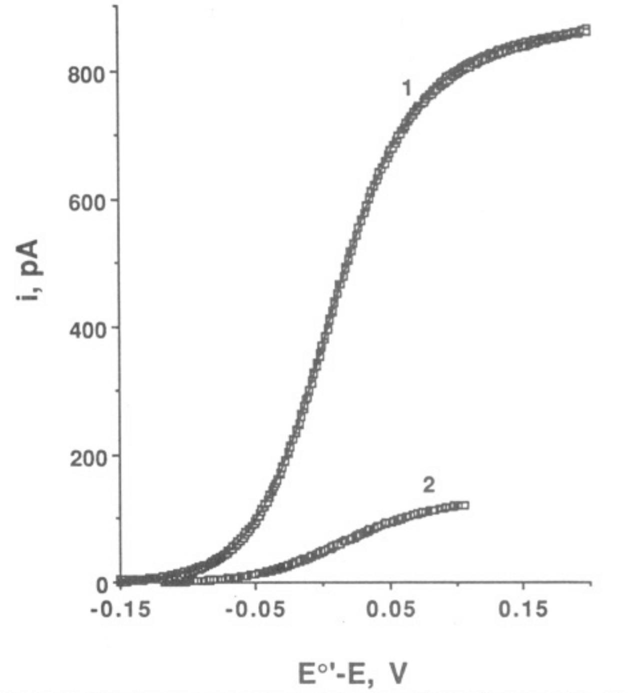

Figure 5. Steady-state voltammograms of the first reduction of C_{60} in (1) ODCB and (2) PhCN in a TLC formed by a 1-μm-radius Pt tip electrode and Hg substrate. v = 20 mV/s. Squares are experimental data, and the solid lines are theoretical curves calculated with eq 9 from ref 14 and the kinetic parameters given in the text. For other parameters, see Figure 2.

in steady-state measurements with the same UME tip electrode by using the SECM. This allows one to study faster electrode processes without many of the difficulties associated with rapid CV. The basic principle employed here has been discussed in connection with our previous experiments in aqueous solutions,[8] in which a Pt tip penetrated the mercury pool and trapped a thin layer of the electrolyte between the tip and the Hg substrate electrodes. This tip/electrolyte/substrate configuration behaves as a twin electrode thin-layer cell (Figure 4) whose thickness l can be evaluated[8] by assuming the equality of the diffusion coefficients of the oxidized and reduced electroactive species.

$$l = \pi a i_{t,\infty}/4i_d \qquad (2)$$

where i_d is the diffusion-limited current in the TLC. The mass-transfer coefficient m for such a TLC, where

$$m = D/l = i_d/nFAc^* \qquad (3)$$

and $A = \pi a^2$ is the tip surface area, can be made appreciably larger than that for the UME in bulk solution (where $m \approx D/a$) when $l \ll a$, allowing faster kinetic measurements. The steady-state TLC voltammograms (Figure 5) yielded $\Delta E_{1/4}$ = 32.6 ± 0.2 mV and $\Delta E_{3/4}$ = 36.6 ± 0.4 mV (ODCB, curve 1); $\Delta E_{1/4}$ = 35.5 ± 0.5 mV and $\Delta E_{3/4}$ = 39.7 ± 0.5 mV (PhCN, curve 2). The thickness of the TLC from eq 2 was about 0.23 and 0.35 μm for curves 1 and 2, respectively. The analysis based on Table I in ref 14 with m values calculated from eq 3 resulted in the following sets of parameters: $\lambda = 2.7 \pm 0.5$, $k^0 = 0.46 \pm 0.08$ cm/s, and $\alpha = 0.43 \pm 0.05$ (ODCB); and $\lambda = 1.35 \pm 0.2$, $k^0 = 0.12 \pm 0.02$ cm/s, and $\alpha = 0.52 \pm 0.05$ (PhCN). Note that the increase in a mass-transfer rate in the TLC arrangement compared to the microdisk steady-state measurements in bulk solution made the electrode reaction apparently less reversible and thus significantly decreased uncertainties in k^0 and α. The values of k^0 found are consistent with the limits obtained from fast CV measurements. The theoretical curves (the solid lines in Figure 5) calculated with the above parameters fit the experimental data very well. The same parameters were used to simulate the microdisk steady-state voltammograms from eq 13 in ref 15 (the solid lines in Figure 3), which are also in a good agreement with the experimental ones. The k^0 value determined in PhCN is close to that found by Fawcett and co-workers.[6] However, a quantitative comparison is difficult because the rate constant in ref 6 was related to the half-wave potential rather than to $E^{0\prime}$. Moreover, the $E^{0\prime}$ and k^0 values can vary somewhat with $TBABF_4$ concentration because of ion pairing.[6]

The rate constant found for the reduction of C_{60} to C_{60}^- appears low when compared with those of much smaller aromatic hydrocarbons in solvents like DMF and MeCN. One would expect little internal reorganization of C_{60} on addition of an electron (i.e., a small λ_i[18]) and a relatively small amount of solvent reorganization (λ_0) because of the large radius of the C_{60} molecule. However, as Opallo and Fawcett[19] point out, solvation effects can be important. Moreover, rather extensive ion pairing of C_{60}^- with TBA^+ ions can occur in these low dielectric constant solvents.[1c,6]

---

(17) Bard, A. J.; Mirkin, M. V.; Unwin, P. R.; Wipf, D. O. *J. Phys. Chem.* **1992**, *96*, 1861.

(18) Marcus, R. A. *J. Chem. Phys.* **1965**, *43*, 679.

(19) Fawcett, W. R.; Opallo, M. *J. Phys. Chem.* **1992**, *96*, 2920.

The differences between the rate constants found in PhCN and ODCB could be attributed to differences in their dielectric properties and dynamics. A quantitative treatment is difficult because of the lack of the necessary data for ODCB in the literature.

Conclusions

We have determined the kinetic parameters and diffusion coefficients for the first reduction of C_{60} in two solvents, 1,2-dichlorobenzene and benzonitrile. The SECM/TLC technique employed combines the capability of quite fast heterogeneous kinetic measurements with the advantages of steady-state methods, i.e., it is free from problems caused by the ohmic drop and charging current and allows for a very simple treatment of the experimental data.

Acknowledgment. The support of this research by the National Science Foundation (CHE 9214480) is gratefully acknowledged. L. O. S. B. acknowledges the support of FAPESP (Fundação de Amparo a Pesquisa do Estado de São Paulo-Brazil). We appreciate the receipt of the paper by R. Fawcett and co-workers before publication.

Chemisorption of Ethylene onto Supported $Pt/\gamma\text{-}Al_2O_3$ and $Ag/\gamma\text{-}Al_2O_3$ As Followed by Solid-State Static and CP/MAS ^{13}C and Static ^{2}H NMR Spectroscopy

Yu-Hsing Chin[†] and Paul D. Ellis*

Contribution from the Department of Chemistry, University of South Carolina, Columbia, South Carolina 29208. *Received October 9, 1990. Revised Manuscript Received July 16, 1992*

Abstract: The adsorption of ethylene onto two metal-supported catalyst systems is reported. The first is Pt on $\gamma\text{-}Al_2O_3$. Here is it found that high-resolution solid-state ^{13}C CP/MAS methods *cannot* be utilized to investigate the structure of the adsorbed species. This arises due to the near ferromagnetic character of platinum metal. However, this problem can be circumvented by examining the solid-state ^{2}H NMR. From this investigations, it is clear that the dominant species on the surface is ethylidyne. These results are discussed in light of the previous work in the area. Ethylene adsorption was also examined for a supported silver system. In this system there are no problems with susceptibility of the metal surface. By utilizing a combination of mono- and dilabeled ^{13}C ethylene, the shielding tensor and the carbon–carbon bond distance of the adsorbed ethylene were deduced.

Introduction

In the past two decades, the adsorptions of alkenes and alkynes onto supported transition metals have been experimentally investigated by a number of high-resolution spectroscopic techniques, such as LEED,[1] infrared,[2] Auger,[3] and so on. In the particular case of ethylene onto supported Pt catalysts, the type of bonding and the associated reactions on the Pt surfaces are of continuing interest in the surface chemistry community. Unfortunately, the structures of these olefins on a Pt surface lead to archetypal problems and remain controversial to date. In the previous studies of ethylene on a Pt single crystal structure, Ibach et al.[4] showed, using EELS and TPDS, that the ethylidyne species formed upon the reaction of C_2H_4 with Pt(III). By utilizing infrared spectroscopy, Malik et al.[5] also concluded that the same species existed on Pt(III). The ethylidyne species on a 10% Pt/Al_2O_3 surface was proposed by Beebe et al.[6] and is consistent with the Bandy et al.[7] study of ethylene on a Pt/SiO_2 surface. However, on the basis of infrared spectroscopy, Prentice et al.[8] postulated a π-complexed form of ethylene on silica-supported Pt surfaces with the $C{=}C$ stretching band near 1500 cm^{-1}, which was in agreement with Soma's[9] infrared study of adsorbed ethylene on 9% Pt/Al_2O_3 at 195 K. Alternatively, from an analysis of the dipolar line shapes on the ^{1}H NMR spectroscopy, Shibanuma et al.[10] ruled out the ethylidyne species and favored a multiply bonded species ($-CH_2CH=$) on unsupported platinum powder. In contrast to chemisorbed acetylene on a platinum catalyst, Slichter et al.[11a] explicitly deduced the structure of adsorbed ethylene by probing the dipolar interactions among the nuclei. They suggested an ethylidyne species ($\equiv C{-}CH_3$) with a C–C bond length of 1.49 ± 0.02 Å. The methyl group ($-CH_3$) on ethylidyne freely rotates about the C–C direction at 77 K. Carbon–carbon bond rupture occurs above 390 K, and the decomposition was completely finished at about 480 K. Later[11b] they confirmed a rotating methyl group by analyzing deuterium powder patterns at 77 K. Furthermore, in a high-resolution solid-state ^{13}C NMR study of the adsorbed ethylene on platinum catalysts, Gay[12] carried out the reaction of adsorbed ethylene on a series of catalyst preparations. In his report, Gay claimed that the adsorbed ethylene reactivity is correlated to the characteristics of Pt catalyst, e.g., the metal particle size, nature of support, and the dispersion of platinum atom. Gay had prepared 5% and 10% Pt on Al_2O_3 and SiO_2 support catalysts, with variable dispersions from 0.23 to 1.30, by adsorption and impregnation methods (with Cl^- ions). He observed a π-bonded olefin species in all catalysts. The π-complexed olefin on $Pt/\gamma\text{-}Al_2O_3$ catalysts in the presence or absence of Cl^- further reacts to form a σ-vinyl group or a species with a $C{=}C$ double

---

[†] Presented as partial fulfillment of the requirements for the degree of Doctor of Philosophy in the Department of Chemistry, University of South Carolina.

(1) Koestner, R. J.; Van Hove, M. A.; Somorjai, G. A. *J. Phys. Chem.* **1983**, *87*, 203.
(2) Beebe, T. P.; Albert, M. R.; Yates, J. T., Jr. *J. Catal.* **1981**, *111*, 441.
(3) Ganning, N. D. S.; Baker, M. D.; Chesters, M. A. *Surf. Sci.* **1982**, *120*, 19.
(4) Steininger, H.; Ibach, H.; Lehwald, S. *Surf. Sci.* **1982**, *117*, 685.
(5) Malik, I. J.; Brubaker, M. E.; Mohsin, S. B.; Trenary, M. *J. Chem. Phys.* **1987**, *87*, 5554.
(6) Beebe, T. P.; Yates, J. T., Jr. *J. Phys. Chem.* **1987**, *91*, 254.
(7) Bandy, B. J.; Chesters, M. A.; James, D. I.; McDougall, G. S.; Pemble, M. E.; Sheppard, N. *Philos. Trans. R. Soc. London, A* **1986**, *318*, 141.
(8) Prentice, J. D.; Lesiunas, A.; Sheppard, N. *J. Chem. Soc., Chem. Commun.* **1976**, 76.
(9) Soma, Y. *J. Catal.* **1979**, *59*, 239.
(10) Shibanuma, T.; Matsui, T. *Surf. Sci.* **1985**, *154*, L215.
(11) (a) Wang, P. K.; Slichter, C. P.; Sinfelt, J. H. *J. Phys. Chem.* **1985**, *89*, 3606. (b) Zax, D. B.; Klug, C. A.; Slichter, C. P.; Sinfelt, J. H. *J. Phys. Chem.* **1989**, *93*, 5009.
(12) Gay, I. D. *J. Catal.* **1987**, *108*, 15.

0002-7863/93/1515-204$04.00/0 © 1993 American Chemical Society