noninteracting substituents. Numerous substrates meeting this criterion have been examined.

The ground-state conformational energy minima of various asymmetrically substituted dialkylbenzenes are experimentally established by matching the number of observed $0_0^0$ origin transitions to the various "geometrical" possibilities. Thus, the ArCH$_2$–C bond of aromatic to primary alkyl substituents, e.g., ethylbenzene $\tau_1$ (in Figure 1) is perpendicular to the plane of the aromatic ring, and the C–H bond in aryl to secondary alkyl bonds (e.g., in isopropylbenzene) is *in* the plane of the aromatic ring. Similarly, jet spectroscopy has established that one of the methyl groups in *tert*-butylbenzene (an example of an aryl to tertiary alkyl bond containing substrate) is *in* the plane of the aromatic ring.

The second torsion of the aromatic alkyl side chain $\tau_2$ (cf. Figure 1) is also established for a number of compounds, including propylbenzenes and butylbenzenes. In these cases, two ground-state minima are observed for each compound. Unfortunately, information regarding the third torsion $\tau_3(C_\alpha–C_\beta–C_\gamma–C_\delta)$ is not obtained in the only compound possessing a $C_\delta$, namely, butylbenzene. The structural variability at $C_\delta$ may be too far removed from the aromatic chromophore in the molecule to allow structural discrimination, even by these sensitive methods.

This work strongly supports our previous conclusions that jet spectroscopy is an excellent technique for the observation and identification of conformations of aromatic molecules which interconvert with very low energy barriers. The experimental observations are complemented by molecular orbital–molecular mechanics (MOMM) calculations which estimate the stabilities of various conformations of these molecules.

## Experimental Section

The time-of-flight mass spectrometer was as described elsewhere.[9] The TOFMS experiment used a R.M. Jordan pulsed valve. Both helium and argon were used as carrier gases, as specified for each experiment. All TOFMS experiments were performed at room temperature, and involved one-color two-photon photoionization.

Dispersed emission (DE) experiments were carried out in a fluorescence excitation chamber described previously.[9] f/4 optics were used to collect and focus the emission onto the slits of an f/8 2051 GCA McPherson 1-m scanning monochromator with a dispersion of 2.78 A/mm in third order of a 1200 groove/mm 1.0-μ blazed grating. Expansion of the gas into the chamber was achieved with a Quanta Ray PSV-2 pulsed valve with a 500-μm pinhole located ~1 cm from the laser beam. Samples were placed in the head of the valve and heated to 65–70 °C to achieve a greater concentration in the jet. Helium at 70 psi was used as the carrier gas except as otherwise noted. The alkylbenzenes 7, **12**, **13**, **15**, **16**, **20**, **21**, **24**, **36**, **40**, **42**, and **45** were purchased from either Aldrich Chemical Co. or Wiley Organics. The purity of these materials was determined by GC and NMR spectroscopy prior to their use. Experimental details for the preparation of **4**, **10**, **11**, **15**, **25**, **26**, and **30** are given in the Supplementary Material.

Empirical force field calculations are performed using the molecular orbital–molecular mechanics (MOMM-85) algorithm of Kao.[14,21] This force field has been specifically parametrized for aromatic ring systems and is known to reproduce experimental geometries and energies. MOMM has also been used to correlate steric energies with the rates of certain aromatic ring additions[22] and pyrolysis reactions.[23] The ground-state calculations are performed using complete geometry optimization to determine the ground-state energy minimum (the stable conformation) and to estimate the potential energy barriers to rotation about the $C_{aromatic}–C_\alpha$ and $C_\alpha–C_\beta$ bonds, i.e., about the torsions $\tau_1(C_{ortho}–C_{ipso}–C_\alpha–C_\beta)$ and $\tau_2(C_{ipso}–C_\alpha–C_\beta–C_\gamma)$, respectively.

**Acknowledgment.** We thank J. Campbell for obtaining the NMR spectra, D. Seal and T. Sinkiewicz for secretarial assistance, R. Ferguson, A. Kassman, B. LaRoy, and C. Lilly for their encouragement and enthusiasm regarding this work, and J. B. Paine III for helpful discussions.

**Registry No.** 7, 538-93-2; **12**, 1007-26-7; **13**, 104-51-8; **16**, 98-82-8; **20**, 535-77-3; **21**, 4920-99-4; **24**, 135-98-8; **25**, 4481-30-5; **26**, 19262-20-5; **36**, 98-06-6; **40**, 7364-19-4; **42**, 1075-38-3; **45**, 1014-60-4; toluene, 108-88-3; ethylbenzene, 100-41-4; propylbenzene, 103-65-1.

**Supplementary Material Available:** Experimental details for the preparation of **4**, **10**, **11**, **15**, **25**, **26**, and **30**, including spectroscopic data and elemental analyses for these compounds (5 pages). Ordering information is given on any current masthead page.

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(21) Kao, J.; Leister, D.; Sito, M. *Tetrahedron Lett.* **1985**, 2403.
(22) Seeman, J. I. *Pure Appl. Chem.* **1987**, *59*, 1661.
(23) Houminer, Y.; Kao, J.; Seeman, J. I. *J. Chem. Soc., Chem. Commun.* **1984**, 1608.

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# Fourier Transform Mass Spectrometric Generation and Studies of Carboethoxycarbene Anion Radical (EtOCOCH$^{\bullet-}$)

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**Abstract:** In contrast to results from flowing afterglow studies, electron attachment with ethyl diazoacetate in a Fourier transform mass spectrometer produces abundant carboethoxycarbene anion radical, EtOCOCH$^{\bullet-}$. Upon collision-induced dissociation, EtOCOCH$^{\bullet-}$ appears to eliminate C$_2$H$_4$ via a six-membered transition state yielding an ion with $m/z$ 58. Two resonance structures, a carbon-centered radical anion (I) and an oxygen-centered anion (II), can be considered in order to understand the reactivity of EtOCOCH$^{\bullet-}$. Reactions of EtOCOCH$^{\bullet-}$ with carbonyl compounds and activated olefins can be rationalized by considering the carbon-centered radical anion (I) to make a greater contribution. With use of the bracketing method, the proton affinity of EtOCOCH$^{\bullet-}$ is determined to be 377.2 ± 2 kcal/mol, from which $\Delta H_f$(EtOCOCH$^{\bullet-}$) = −48.5 ± 3 kcal/mol was calculated. As a free radical, EtOCOCH$^{\bullet-}$ abstracts H$^\bullet$ atoms from various H$^\bullet$ atom donors. Using such reactions to bracket the hydrogen dissociation energy yields an estimate of $D$(EtOCOCH$^-$H) ≥ 101 ± 1 kcal/mol.

Photolytic decomposition of diazo compounds is widely used in synthetic organic chemistry for generating carbene intermediates.[1] Because these latter species possess unfilled electronic valence levels, they are very reactive, and undergo a variety of addition and insertion reactions. Although interest in the structure, stability, and reactivity of carbenes has stimulated extensive studies during the last several decades, the anionic analogues of carbenes have received attention only recently.

Both gas-phase[2,3] and condensed-phase[4,5] studies suggest that

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(1) (a) Jones, M., Jr.; Moss, R. A. *Carbenes*; Wiley: New York, 1973; Vol. I and II. (b) Kirmse, W. *Carbene Chemistry*, 2nd ed.; Academic Press: New York, 1971.
(2) Zittel, P. F.; Ellison, G. B.; O'Neil, S. V.; Herbst, E.; Lineberger, W. C.; Reinhardt, W. P. *J. Am. Chem. Soc.* **1976**, *98*, 3731–3732.
(3) McDonald, R. N.; Chowdhury, A. K.; Setser, D. W. *J. Am. Chem. Soc.* **1980**, *102*, 6491–6498.

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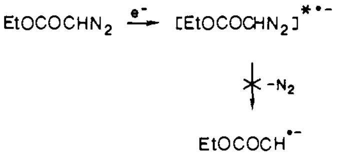
certain diazoalkane anion radicals undergo unimolecular loss of nitrogen to generate the corresponding carbene anion radicals. In the condensed phase, carbene anion radicals, produced by electrochemical reduction of diazoalkanes, readily react with the solvent. Thus, one's ability to characterize reactivity of such anions in solution is limited. However, gas-phase studies offer a number of advantages for study of carbene anion radicals. For example, a radical anion of interest ($R_2C^{\bullet-}$) can be generated cleanly via dissociative electron attachment to the appropriate diazo precursor (eq 1) in a solvent-free system and a variety of neutral reagents can be added to examine its reactivity.

$$\mathrm{R_2C{=}N_2 + e^- \rightarrow R_2C^{\bullet-} + N_2} \qquad (1)$$

Rapid and significant progress in understanding gas-phase carbene[3,6] and nitrene[7] radical anion chemistry over the last eight years has promoted new insights into the properties and reactivities of these important classes of reactive species. It is now believed that both carbene and nitrene anion radicals, unless other extremely exothermic reaction channels are available, undergo nucleophilic carbonyl addition followed by radical $\beta$-fragmentation. Such nucleophilic addition reactions with carbonyl compounds as well as $H^\bullet$ atom abstraction reactions with potential $H^\bullet$ atom donors may be utilized to characterize open-shell carbene and nitrene anion radicals. Recently, DePuy and co-workers[8] demonstrated a new gas-phase method for generation of carbene anion radicals. They utilized a selected ion flow tube (SIFT) to isolate methylidene anion radical ($CH_2^{\bullet-}$) from a series of anions produced by electron ionization of methane.

Although generation of carbene anion radicals from diazoalkanes is a well-established procedure, a major exception to the generality of this reaction was reported recently.[9] Of particular interest is the observation that ethyl diazoacetate anion radical was the exclusive product (eq 2) in a flowing afterglow (FA)



$$\begin{array}{ccccc}\mathrm{EtOCOCHN_2} & \xrightarrow{e^-} & [\mathrm{EtOCOCHN_2}]^{*\bullet-} & \longrightarrow & \mathrm{EtOCOCHN_2}^{\bullet-} \\ & & \not\downarrow\ {-\mathrm{N_2}} & & \\ & & \mathrm{EtOCOCH}^{\bullet-} & & \end{array} \qquad (2)$$

system. Failure to lose $N_2$ from this intermediate diazo anion radical suggests that collisional stabilization in the FA system is an efficient process. It occurred to us that, under the low-pressure conditions (ca. $10^{-7}$ Torr) prevailing in the trapped ion cell of a Fourier transform mass spectrometer (FTMS), collisional stabilization of excited ethyl diazoacetate anion radicals may not be a competitive process, compared with unimolecular decomposition, losing $N_2$ to generate carboethoxycarbene anion radical. Here we report that ethyl diazoacetate indeed does undergo dissociative electron attachment, yielding abundant carboethoxycarbene anion radical, under FTMS conditions. Its reactions have been qualitatively characterized and the proton affinity (PA), $H^\bullet$ atom affinity (HA), electron affinity (EA), and heats of formation of the carboethoxycarbene anion radical determined.

## Experimental Section

The theory and instrumentation of Fourier transform mass spectrometry are well documented in the literature.[10] All experiments in this work were performed using a Nicolet FTMS-1000 Fourier transform mass spectrometer equipped with a 5.08-cm cubic trapping cell and 3.0-tesla superconducting solenoid magnet. To retain negative ions in the cell, a potential of −0.7 V was applied to the trap plates. In a typical experiment sequence, ethyl diazoacetate was introduced into the FTMS system immediately after a freeze–pump–thaw cycle. Carboethoxycarbene anion radical was generated by a 200-ms beam of 0.199-eV electrons with a filament emission current of approximately 1–2 mA. $\mathrm{EtOCOCH}^{\bullet-}$ anions were trapped in the cell for variable times (from a few milliseconds to several seconds) to allow ion–molecule reactions with the selected neutral reagent gas. The sequence was then repeated to coadd about 50 spectra. The diazo ester appeared to decompose in the expansion volume since, within a few minutes, no carboethoxycarbene anion radical ($m/z$ 86) could be observed. At this point the only observed anion was one with $m/z$ 172, probably diethyl maleate anion. Since no decomposition was observed in a glass inlet,[11] metal-catalyzed decomposition to yield $N_2$ might be responsible for instability of the starting ethyl diazoacetate under the experimental conditions. Reaction of carboethoxycarbene with the diazo ester in the metal inlet could produce diethyl maleate (eq 3) which subsequently could attach an electron in the FTMS cell, to produce diethyl maleate anion (eq 4).

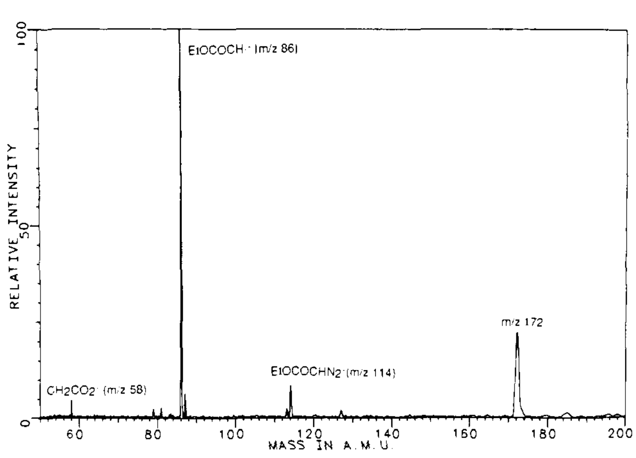


**Figure 1.** Low resolution negative ion FT mass spectrum of ethyl diazoacetate.

$$\mathrm{EtOCOCH{:} + EtOCOCHN_2 \rightarrow EtOCOCH{=}CHCOOEt + N_2} \qquad (3)$$

$$\mathrm{EtOCOCH{=}CHCOOEt + e^- \rightarrow} \underset{m/z\ 172}{\mathrm{EtOCOCHCHCO_2Et^{\bullet-}}} \qquad (4)$$

Because of these circumstances, the metal inlet system was pumped out after collection of each set of coadded spectra and fresh ethyl diazoacetate introduced for the next experiment.

Gas and liquid reagents used were purchased from commercial sources (Liquid Carbonics and Aldrich). Deuterated alcohols were obtained from Aldrich. Reagents were used as supplied, after multiple freeze–pump–thaw degassing cycles to remove noncondensable gases.

## Results and Discussion

Dissociative electron attachment with $\mathrm{EtOCOCHN_2}$ in the FTMS yields abundant carboethoxycarbene anion radical, $m/z$ 86 (see Figure 1). This is in contrast to high-pressure FA results[9] where exclusive formation of molecular diazo anion radical was observed. Flowing afterglow systems operate at relatively high pressures (0.3–1.0 Torr), the electron energy distribution is significantly broader, and fragmentation of the molecular ion is less evident. Furthermore, multiple collisions with He buffer gas allow collisional stabilization of vibrationally excited molecular ions. Such stabilization is inefficient in the low-pressure FTMS system, and fragmentation of molecular ions is more likely. The minor amount of ethyl diazoacetate anion radical ($m/z$ 114) detected in the mass spectrum (Figure 1) probably results from collisional stabilization of the excited diazo anion. Two resonance structures

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(4) (a) McDonald, R. N.; January, J. R.; Borhani, K. J.; Hawley, M. D. *J. Am. Chem. Soc.* **1977**, *99*, 1268–1270. (b) Van Galen, D. A.; Young, M. P.; Hawley, M. D.; McDonald, R. N. *J. Am. Chem. Soc.* **1985**, *107*, 1465–1470.

(5) (a) Bethel, D.; Parker, V. D. *J. Am. Chem. Soc.* **1986**, *108*, 895–900. (b) Bethel, D.; Parker, V. D. *J. Am. Chem. Soc.* **1986**, *108*, 7194–7200.

(6) (a) McDonald, R. N.; Chowdhury, A. K.; McGhee, W. D. *J. Am. Chem. Soc.* **1984**, *106*, 4112–4116. (b) McDonald, R. N.; Gung, W. Y. *J. Am. Chem. Soc.* **1987**, *109*, 7328–7334.

(7) (a) McDonald, R. N.; Chowdhury, A. K. *J. Am. Chem. Soc.* **1981**, *103*, 674–676. (b) Pellerite, M. J.; Brauman, J. I. *J. Am. Chem. Soc.* **1981**, *103*, 676–677. (c) McDonald, R. N.; Chowdhury, A. K. *J. Am. Chem. Soc.* **1980**, *102*, 6146–6147. (d) McDonald, R. N., Chowdhury, A. K. *J. Am. Chem. Soc.* **1983**, *105*, 198–207.

(8) DePuy, C. H.; Barlow, S. E.; Van Doren, J. M.; Roberts, C. R.; Bierbaum, V. M. *J. Am. Chem. Soc.* **1987**, *109*, 4414–4415.

(9) McDonald, R. N.; Chowdhury, A. K. *Tetrahedron* **1986**, *42*, 6253–6262.

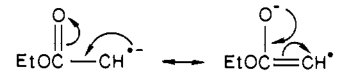
(10) (a) Comisarow, M. B.; Marshall, A. G. *Chem. Phys. Lett.* **1974**, *25*, 282–283. (b) Comisarow, M. B.; Marshall, A. G. *Chem. Phys. Lett.* **1974**, *26*, 489–490. (c) Ghaderi, S.; Kulkarani, P. S.; Ledford, E. B., Jr.; Wilkins, C. L.; Gross, M. L. *Anal. Chem.* **1981**, *53*, 428–437. (d) Wilkins, C. L.; Gross, M. L. *Anal. Chem.* **1981**, *53*, 1661A–1676A. (e) Gross, M. L.; Rempel, D. L. *Science* **1984**, *226*, 261–268.

(11) McDonald, R. N., private communication.

Table I. Summary of Product Data for the Ion–Molecule Reactions of the Carboethoxy Anion Radical (EtOCOCH$^{\bullet}$)

| ion + neutral reactions | | primary products [assumed neutral] | branching ratio |
|---|---|---|---|
| $EtOCOCH^{\bullet-} + EtOCOCHN_2$ | → | $EtOCOCH_2^-[+EtOCOCN_2]$ | 0.67 |
| | → | $EtOCOCN_2^-[+EtOCOCH_2]$ | 0.08 |
| | → | $EtOCOCH{=}CHCO_2Et^-[+N_2]$ | 0.25 |
| $EtOCOCH^{\bullet-} + CH_3NO_2$ | → | $O_2NCH_2^-[+EtOCOCH_2^{\bullet}]$ | 1.00 |
| $EtOCOCH^{\bullet-} + (CH_3)_3COH$ | → | $(CH_3)_3CO^-[+EtOCOCH_2^{\bullet}]$ | 1.00 |
| $EtOCOCH^{\bullet-} + CH_3CN$ | → | $EtOCOCH_2^-[+NCCH_2^{\bullet}]$ | 1.00 |
| $EtOCOCH^{\bullet-} + C_2H_5OH$ | → | $C_2H_5O^-[+EtOCOCH_2^{\bullet}]$ | 0.52 |
| | → | $EtOCOCH_2^-[+C_2H_5O^{\bullet}]$ | 0.48 |
| $EtOCOCH^{\bullet-} + C_2H_5OD$ | → | $C_2H_5O^-[+EtOCOCHD^{\bullet}]$ | 0.55 |
| | → | $EtOCOCHD^-[+C_2H_5O^{\bullet}]$ | 0.29 |
| | → | $EtOCOCD_2^-$ | 0.16 |
| $EtOCOCH^{\bullet-} + CH_3OH$ | → | $EtOCOCH_2^-[+CH_3O^{\bullet}]$ | 1.00 |
| $EtOCOCH^{\bullet-} + CH_3OD$ | → | $EtOCOCHD^-[+CH_3O^{\bullet}]$ | 1.00 |
| $EtOCOCH^{\bullet-} + C_6H_5CH_3$ | → | no reaction | |
| $EtOCOCH^{\bullet-} + C_6H_5C_2H_5$ | → | no reaction | |
| $EtOCOCH^{\bullet-} + CH_3COCH_3$ | → | $CH_3COCH_2^-[+EtOCOH_2^{\bullet}]$ | 0.14 |
| | → | $EtOCOCH_2^-[+CH_3COCH_2^{\bullet}]$ | 0.77 |
| | → | $EtOCOCHCOCH_3^-[+^{\bullet}CH_3]$ | 0.09 |
| $EtOCOCH^{\bullet-} + C_6H_6COC_6H_5$ | → | $EtOCOCHCOC_6H_5^-[+^{\bullet}C_6H_5]$ | 0.95 |
| | → | $C_6H_5COC_6H_5^{\bullet-}[+EtOCOCH{:}]$ | 0.05 |
| $EtOCOCH^{\bullet-} + C_6H_5CH{=}CHCHO$ | → | $C_6H_5CH{=}CHCHO^{\bullet-}[+EtOCOCH{:}]$ | 0.42 |
| | → | $EtOCOCHCOCH{=}CHC_6H_5^-[+^{\bullet}H]$ | 0.32 |
| | → | $EtOCOCHCHO^-[+C_6H_5CH{=}CH^{\bullet}]$ | 0.16 |
| | → | $EtOCOCHCHCHC_6H_5^-[+^{\bullet}HCO]$ | 0.10 |
| $EtOCOCH^{\bullet-} + CH_2CH_2$ | → | no reaction | |
| $EtOCOCH^{\bullet-} + CH_2{=}CHCN$ | → | $C_3H_2CH^-[+EtOCOCH_2^{\bullet}]$ | 0.42 |
| | → | $EtOCOCH\text{-}CH{=}CHCN^-[+^{\bullet}H]$ | 0.58 |
| $EtOCOCH^{\bullet-} + CH_2CHCO_2CH_3$ | → | $EtOCOCHCHCHCO_2CH_3^-[+^{\bullet}H]$ | 0.18 |
| | → | $EtOCOCHCOCHCH_2^-[+^{\bullet}OCH_3]$ | 0.82 |
| $EtOCOCH^{\bullet-} + CF_3CO_2CH_3$ | → | $EtOCOCHCOCF_3^-[+^{\bullet}OCH_3]$ | 0.99 |
| | → | $EtOCOCHCO_2CH_3^-[+^{\bullet}CF_3]$ | 0.01 |
| $EtOCOCH^{\bullet-} + CF_3CO_2C_2H_5$ | → | $EtOCOCHCOCF_3^-[+^{\bullet}OCH_3]$ | 0.99 |
| | → | $EtOCOCHCO_2C_2H_5[+^{\bullet}CF_3]$ | 0.10 |
| $EtOCOCH^{\bullet-} + CH_3Cl$ | → | $Cl^-[+EtOCOCHCH_3]$ | 1.00 |
| $EtOCOCH^{\bullet-} + CH_3Br$ | → | $Br^-[+EtOCOCHCH_3]$ | 1.00 |
| $EtOCOCH^{\bullet-} + C_6F_6$ | → | $C_6F_6^{\bullet-}[+EtOCOCH{:}]$ | 1.00 |
| $EtOCOCH^{\bullet-} + NO_2$ | → | $NO_2^-[EtOCOCH{:}]$ | 1.00 |
| $EtOCOCH^{\bullet-} + CS_2$ | → | $EtOCOCHS^-[+^{\bullet}CS]$ | 1.00 |
| $EtOOCH^{\bullet-} + CO_2$ | → | no reaction | |
| $EtOCOCH^{\bullet-} + O_2$ | → | no reaction | |
| $EtOCOCH^{\bullet-} + N_2O$ | → | no reaction | |
| $EtOCOCH^{\bullet-} + c\text{-}C_3H_6$ | → | no reaction | |

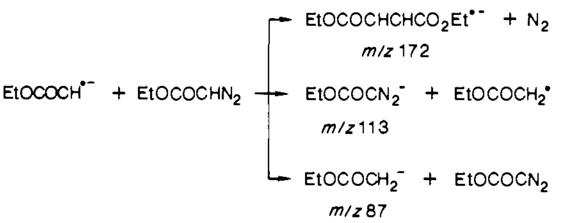
may be considered for EtOCOCH$^{\bullet-}$: (I) carbon-centered radical anion and (II) oxygen-centered anion. Ion–molecule reactions



I II

and product data for EtOCOCH$^{\bullet-}$ are summarized in Table I. A typical pseudo-first-order decay plot for reaction of EtOCOCH$^{\bullet-}$ with $CF_3CO_2CH_3$ is shown in Figure 2.

EtOCOCH$^{\bullet-}$ undergoes a fast reaction with excess ethyl diazoacetate, yielding a number of products (eq 5). Formation



(5)

of the nitrogen displacement product with m/z 172 is analogous to the formation of olefins from triplet methylenes reacting with diazoalkanes.[1] McDonald, Chowdhury, and Setser[3] have demonstrated that carbene anion radicals react with their neutral diazo precursors to yield olefin anion radicals. Such species are believed to be formed by addition of the carbene anion radical at $C_\alpha$ of the diazo compound with subsequent loss of $N_2$. However, in the present study, carboethoxycarbene anion radical failed to react at $N_\beta$ of the diazo ester to form an azine anion radical. The product with m/z 113 is the result of proton abstraction by EtOCOCH$^{\bullet-}$. This establishes that carboethoxycarbene anion radical is basic enough to abstract a proton from ethyl diazoacetate.

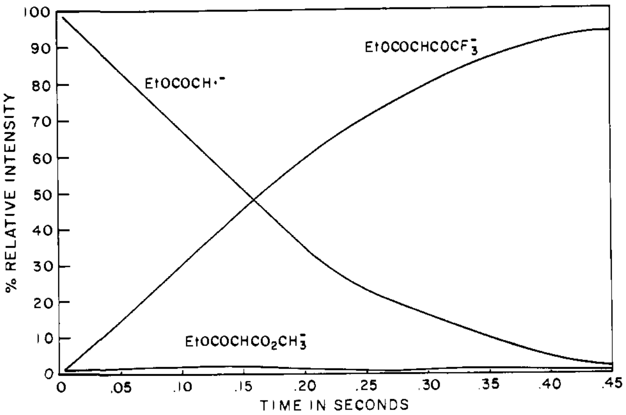


Figure 2. Ion intensities as percent of total ion current of carboethoxycarbene anion radical and ionic reaction products as a function of time, with $CF_3CO_2CH_3$; pressure ($CF_3CO_2CH_3$) = $1.0 \times 10^{-7}$ Torr.

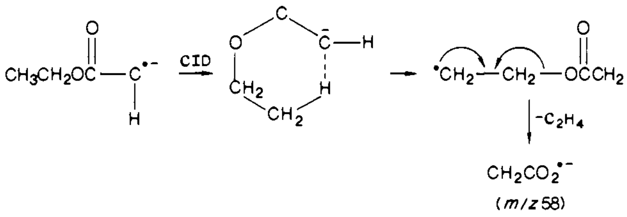
Electron ionization of ethyl diazoacetate also consistently produced a minor product with m/z 58. When the carboethoxycarbene anion radical (m/z 86) is collisionally activated in the presence of air, increasing the translational energy for collisional activation results in an increase in the abundance of the

Table II. Data for Bracketing Proton Affinity of $EtOCOCH^{\bullet -}$

| reaction | | product ion | proton transfer | $\Delta H_{acid}$[a] (kcal/mol) |
|---|---|---|---|---|
| $EtOCOCH^{\bullet -} + CH_3NO_2$ | $\rightarrow$ | $O_2NCH_2^- + EtOCOCH_2^\bullet$ | yes | 358.7 |
| $EtOCOCH^{\bullet -} + CH_3COCH_3$ | $\rightarrow$ | $CH_3COCH_2^- + EtOCOCH_2^\bullet$ | yes | 368.8 |
| $EtOCOCH^{\bullet -} + CH_3CN$ | $\not\rightarrow$ | $NCCH_2^- + EtOCOCH_2^\bullet$ | no | 372.2 |
| $EtOCOCH^{\bullet -} + (CH_3)_3COH$ | $\rightarrow$ | $(CH_3)_3CO^- + EtOCOCH_2^\bullet$ | yes | 373.3 |
| $EtOCOCH^{\bullet -} + C_2H_5OH$ | $\rightarrow$ | $C_2H_5O^- + EtOCOCH_2^\bullet$ | yes | 376.1 |
| $EtOCOCH^{\bullet -} + CH_3OH$ | $\not\rightarrow$ | $CH_3O^- + EtOCOCH_2^\bullet$ | no | 379.2 |
| $EtOCOCH^{\bullet -} + C_6H_5CH_3$ | $\not\rightarrow$ | $C_6H_5CH_2^- + EtOCOCH_2^\bullet$ | no | 378.3 |

[a] Reference 15.

Scheme I



m/z 58 anion. Accurate mass measurements of both the m/z 58 and m/z 86 anions suggest a loss of $C_2H_4$ (mass = 28.0313) instead of CO (mass = 27.9949). Elimination of $C_2H_4$ probably proceeds via a six-membered transition state, as outlined in Scheme I, where internal $H^\bullet$ atom abstraction from the methyl group produces a radical center which then fragments with loss of $C_2H_4$ to yield $C_2H_2O_2^{\bullet -}$.

## Proton Affinity (PA) of $EtOCOCH^{\bullet -}$

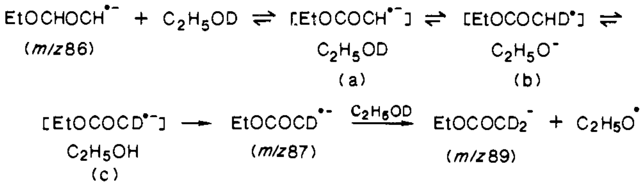
Proton affinity data for an anion radical can be related to other thermochemical values to derive new thermochemical data. Initial studies were, therefore, directed toward determination of the proton affinity of carboethoxycarbene anion radical. To determine the PA, the reactions of $EtOCOCH^{\bullet -}$ with a series of potential proton donors of known gas-phase acidity were investigated. The data pertaining to $H^+$ transfer are given in Table II. $H^+$ transfer was judged to have occurred by observation of the ion signal corresponding to the conjugate base of the added proton donor, as well as by the standard double resonance method.[12] In Table II, two transitions between $H^+$ transfer and no proton transfer are observed; the first is between $CH_3COCH_3$ and $CH_3CN$ and the second between $C_2H_5OH$ and $CH_3OH$. Absence of $H^+$ transfer from $CH_3CN$ suggests that $H^+$ transfer from this carbon acid is slow compared to competing much faster H atom abstraction process. It has recently been suggested[9] that slow $H^+$ transfer may not be observed if other fast reaction channels are available. Furthermore, Farneth and Brauman[13] and Lifshitz and coworkers[14] have shown that many carbon acids undergo slow proton transfer reactions. Thus, the PA of carboethoxycarbene anion radical was bracketed between $\Delta H_{acid}$[15] of $C_2H_5OH$ and $CH_3OH$ giving PA($EtOCOCH^{\bullet -}$) = 377.7 ± 2 kcal/mol. From the relationship[15] $\Delta H_f(EtOCOCH^{\bullet -}) = PA(EtOCOCH^{\bullet -}) + \Delta H_f(EtOCOCH_2^\bullet) - \Delta H_f(H^+)$, $\Delta H_f(EtOCOCH^{\bullet -}) = -48.5 \pm 3$ kcal/mol is calculated, using $\Delta H_f(EtOCOCH_2^\bullet) = -59.1$ kcal/mol[17] and $\Delta H_f(H^+) = 367.2$ kcal/mol.[16]

Table III. Reactions of $EtOCOCH^{\bullet -}$ with Potential H-Atom Donors Used to Bracket $D°(EtOCOCH^- - H)$

| neutral R—H[a] | H-atom transfer | $D°(R-H)$[b] |
|---|---|---|
| $NCCH_2-H$ | yes | 92.9 ± 2.5 |
| $CH_3C(=O)CH_2CH_2-H$ | yes | 98 ± 2.6 |
| $C_2H_5O-H$ | yes | 104 ± 1 |
| $CH_3O-H$ | yes | 104 ± 1<br>101.3 ± 1[e]<br>100.9 ± 1[f] |
| t-BuO—H | no | 105.1 ± 1<br>102.8 ± 1[e] |
| $CH_3-H$ | no | 104.8 ± 0.3 |
| $c\text{-}C_3H_5-H$ | no | 106.3 ± 0.25[c] |
| $CH_2=CH-H$ | no | ≥108[d] |
| $PhCH_2-H$ | no | 87 |

[a] Data taken from Table I. [b] Reference 15. [c] Reference 22. [d] Reference 23. [e] Reference 30. [f] Reference 31.

Scheme II



$$\underset{(m/z\,86)}{EtOCHOCH^{\bullet -}} + C_2H_5OD \rightleftharpoons \underset{(a)}{\left[\begin{matrix}EtOCOCH^{\bullet -}\\ C_2H_5OD\end{matrix}\right]} \rightleftharpoons \underset{(b)}{\left[\begin{matrix}EtOCOCHD^{\bullet}\\ C_2H_5O^-\end{matrix}\right]} \rightleftharpoons$$

$$\underset{(c)}{\left[\begin{matrix}EtOCOCD^{\bullet -}\\ C_2H_5OH\end{matrix}\right]} \longrightarrow \underset{(m/z\,87)}{EtOCOCD^{\bullet -}} \xrightarrow{C_2H_5OD} \underset{(m/z\,89)}{EtOCOCD_2^-} + C_2H_5O^\bullet$$

## Hydrogen Atom and Electron Affinity of $EtOCOCH^{\bullet -}$

The radical behavior of carboethoxycarbene anion radical may be probed by its H atom abstraction reactions with a series of potential H atom donors. The results of such H atom abstraction reactions are listed in Table III. Although reasonably fast H atom abstraction from $CH_3CN$ ($D(NCCH_2-H) = 92.9 \pm 2.5$ kcal/mol[15]) and $CH_3COCH_3$ ($D(CH_3COCH_2-H) = 98 \pm 2.6$ kcal/mol[15]) is observed, $EtOCOCH^{\bullet -}$ failed to react with $CH_4$ ($D(CH_3-H) = 104.9 \pm 0.5$ kcal/mol[21]), $c\text{-}C_3H_6$ ($D(c\text{-}C_3H_5-H) = 106.3$ kcal/mol[22]), and $CH_2=CH_2$ ($D(CH_2=CH-H) > 108$ kcal/mol[23]). Failure of the radical anion to abstract H from nonpolar $CH_4$, $c\text{-}C_3H_6$, and $CH_2=CH_2$ either suggests that these reactions are endothermic or that there are barriers to H atom transfer. The absence of reaction with toluene ($D(PhCH_2-H) = 85 \pm 1$ kcal/mol)[15] also suggests that there are significant barriers to the H atom transfer reaction.

Although the C-H bonds in $CH_3OH$ ($D(H-CH_2OH) = 94 \pm 2$ kcal/mol)[24] and $C_2H_5OH$ ($D(H-CH(CH_3)OH) = 93 \pm 1.0$ kcal/mol)[24] are weaker than the corresponding O-H bond (D-

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(12) (a) Comisarow, M. B.; Grassi, V.; Parisod, G. *Chem. Phys. Lett.* **1978**, *57*, 413-416. (b) Comisarow, M. B. *Adv. Mass Spectrom.* **1980**, *8*, 1698-1706.

(13) Farneth, W. E.; Brauman, J. I. *J. Am. Chem. Soc.* **1976**, *98*, 7891-7897.

(14) Lifshitz, C.; Wu, R. L. C.; Tiernan, T. O. *J. Am. Chem. Soc.* **1978**, *100*, 2040-2048.

(15) Bartmess, J. E.; McIver, R. T., Jr. In *Gas Phase Ion Chemistry*; Bowers, M. T., Ed.; Academic Press: New York, 1979; Vol. 2, Chapter 11.

(16) Stull, D. R.; Prophet, H. *JANAF Thermochemical Tables* (Natl. Stand. Ref. Data Ser., Natl. Bur. Stand., NSRDS-NBS 37) U.S. Government Printing Office: Washington, D.C., 1971.

(17) Heats of formation of $EtOC(=O)CH_2^\bullet$ are calculated using the equation:[15] $\Delta H_f(EtOCOCH_2^\bullet) = D(EtOCOCH_2-H)^{18} - \Delta H_f(H^\bullet)^{19} + \Delta H_f(EtOCOCH_3)$.[20]

(18) Assuming $D(C_2H_5OC(=O)CH_2-H) = D(CH_3OC(=O)CH_2-H) = 98.9 \pm 3$ kcal/mol.[15]

(19) Benson, S. W. *Thermochemical Kinetics*, 2nd ed.; Wiley-Interscience: New York, 1976.

(20) Stull, D. R.; Westrum, E. F., Jr.; Sinke, G. C. *The Chemical Thermodynamics of Organic Compounds*; Wiley: New York, 1969.

(21) Baghal-Vayjooee, M. H.; Colussi, A. J.; Benson, S. W. *J. Am. Chem. Soc.* **1978**, *100*, 3214-3215.

(22) Baghal-Vayjooee, M. H.; Benson, S. W. *J. Am. Chem. Soc.* **1979**, *101*, 2838-2840.

(23) O'Neal, H. E.; Benson, S. W. In *Free Radicals*; Kochi, J. K., Ed.; Wiley: New York, 1973; Vol. 2.

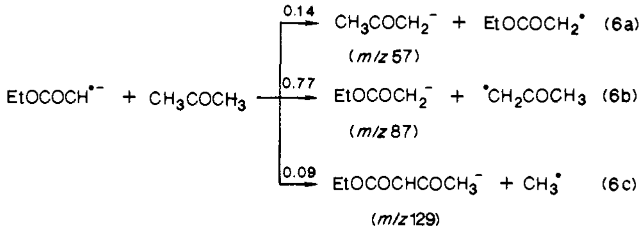
(24) Weast, R. C., Ed. *CRC Handbook of Chemistry and Physics*, 64th ed.; CRC Press: Boca Raton, FL, 1983-1984.

(RO–H) = 104 ± 1 kcal/mol for R = $CH_3$ and $C_2H_5$)[15], deuterium-labeling studies revealed exclusive H atom abstraction from O–H. McDonald and co-workers[3] earlier reported similar observations with cyclopentadienylidene anion radical and suggested that such reactions with alcohols proceed via hydrogen-bonded anion–alcohol complexes. Formation of a similar hydrogen-bonded complex between the carboethoxycarbene anion radical and alcohols could reduce or eliminate barriers to reaction, facilitating abstraction of H from O–H. However, competitive $H^+$ transfer and H-atom abstraction could occur within the same anion–alcohol complex ($EtOCOCH\cdots H\cdots OR^-$) to yield $RO^-$ and $EtOCOH_2^-$. The competitive formation of $RO^-$ and $EtOCOCH_2^-$ would then be controlled by the bond energy of the complexed OH bond and the PA of $RO^-$. If we consider the formation of a second collision complex ($EtOCOCH_2\cdots OR^-$) by a proton transfer within the anion–alcohol complex, the relative electron affinities of $EtOCOCH_2^{\bullet}$ and $^{\bullet}OR$ would then control the relative yields of $EtOCOCH_2^-$ and $OR^-$. For example, such a mechanism could explain the exclusive formation of $EtOCOCH_2^-$ in the reaction of $CH_3OH$ (EA($EtOCOCH_2^{\bullet}$) = 41.5 ± 1.4 kcal/mol[32] > EA($CH_3^{\bullet}$) = 36.2 ± 0.5 kcal/mol[31]). Although a similar argument could be made for the reaction products observed with $C_2H_5OH$, the formation of a significant abundance of the *m/z* 89 with $C_2H_5OD$ is interesting. A plausible mechanism to explain its formation is outlined in Scheme II.

$EtOCOCH^{\bullet-}$ presumably undergoes H/D exchange with $C_2H_5OD$ via multiple proton transfers within long-lived ion–molecule complexes,[25] producing $EtOCOCD^{\bullet-}$. First an ion–molecule complex ($EtOCOCH^{\bullet-}/DOC_2H_5$) a is generated which then undergoes deuteron transfer to generate the second ion/molecule complex ($EtOCOCHD/C_2H_5O^-$) b. Subsequently deuteron or proton transfer takes place to form complex a or c, which then can dissociate into the reactants or H/D-exchanged products ($EtOCOCD^{\bullet-}$ (*m/z* 87) and $C_2H_5OH$), respectively. The anion *m/z* 87 then abstracts a D atom from a second $C_2H_5OD$ molecule to form the observed $EtOCOCD_2^-$ (*m/z* 89) anion. Interestingly, the *m/z* 89 anion was not observed as a product of reaction with $CH_3OD$, probably due to nonoccurrence of the initial proton transfer reaction. No H atom abstraction reaction was observed with *tert*-butyl alcohol (*D*(*t*-BuO–H) = 105.1 ± 1.0 kcal/mol).[15] Because $H^+$ transfer from *t*-BuOH occurs rapidly, it is possible that this prevents observation of the slower H atom abstraction reaction. By considering the bond energies of potential proton donors in Table III and energy barriers which might exist in an H atom transfer reactions, we estimated *D*($EtOCOCH^-$–H) > 101 ± 1 kcal/mol. $EtOCOCH^{\bullet-}$ reacts with $NO_2$ (EA = 53.3 kcal/mol)[26] by electron transfer, forming $NO_2^-$. The observed electron transfer reaction with $C_6F_6$ is slow and establishes that EA(EtOCOCH) < 41 kcal/mol.[27]

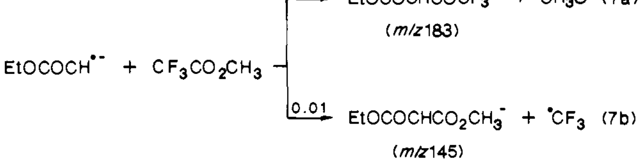
### Reactions of $EtOCOCH^{\bullet-}$ with Carbonyl-Containing Molecules

Reactions of carbene radical anion with carbonyl-containing molecules are interesting because the radical anion could undergo carbonyl addition/radical β-fragmentation in competition with other reaction channels. $EtOCOCH^{\bullet-}$ is expected to react similarly if it is considered to react as a carbon-centered radical anion. The gas-phase reaction of $EtOCOCH^{\bullet-}$ with $CH_3COCH_3$ yields three product anions, with *m/z* 57, 87, and 129, reactions 6a–c. The



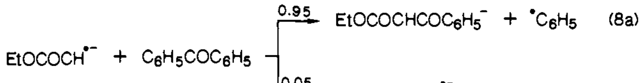
ion with *m/z* 57 is considered to be the conjugate base of acetone, formed by proton transfer to $EtOCOCH^{\bullet}$. The major product derives from hydrogen atom abstraction. The minor product anion (*m/z* 129) appears to result from carbonyl addition followed by loss of $^{\bullet}CH_3$. Thus, the multifaceted reactivities of the carboethoxycarbene anion radical, as a base, free radical, and nucleophile, are clearly observed in its gas-phase reaction with acetone.

When methyl trifluoroacetate is allowed to react with $EtOCOCH^{\bullet-}$, two product anions are observed (reactions 7a and 7b).



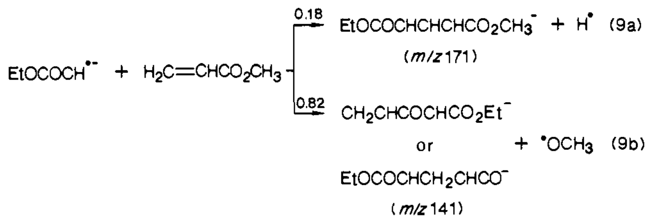
It appears that the major product results from carbonyl addition of $EtOCOCH^{\bullet-}$ to methyl trifluoroacetate followed by radical β-fragmentation of the methoxyl radical. The minor product is probably formed via loss of $CF_3^{\bullet}$ from the tetrahedral intermediate produced by the carbonyl addition reaction. The analogous reaction with ethyl trifluoroacetate produced products of carbonyl addition/radical β-fragmentation in a ratio similar to that observed for the methyl ester.

Because $H^+$ and H atom abstraction from diphenyl ketone is endothermic, reaction of $EtOCOCH^{\bullet-}$ with this substrate is of interest. As expected, the major reaction channel is carbonyl addition, followed by phenyl radical loss (reaction 8a). The minor product $C_6H_5COC_6H_5^{\bullet-}$ (reaction 8b) results from a single electron transfer, presumably yielding the neutral carboethoxycarbene.



### Reactions of $EtOCOCH^{\bullet-}$ with Olefins

Although no reaction was observed with $CH_2{=}CH_2$, $EtOCOCH^{\bullet-}$ reacts rapidly with acrylonitrile, yielding $C_3H_2CN^-$ (42%) and $EtOCOCHCHCHCN^-$ (58%) by proton transfer and 1,4-addition, respectively. Reaction 9a shows an analogous 1,4-



addition/fragmentation reaction observed with methyl acrylate. Two different reactions could result in negative ions with *m/z* 141 (reaction 9b). Radical 1,4-addition/fragmentation or 1,2-addition/fragmentation would yield the products indicated. Although it is verified that carbonyl addition/fragmentation is the favored reaction pathway for $PhN^{\bullet-}$, it is not known which path would

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[25] Squires, R. R.; Bierbaum, V. M.; Gabowski, J. J.; DePuy, C. H. *J. Am. Chem. Soc.* **1983**, *105*, 5185–5192.

[26] Grimsrud, E. P.; Caldwell, G.; Chowdhury, S.; Kebarle, P. *J. Am. Chem. Soc.* **1985**, *107*, 4627–4634.

[27] (a) Lifshitz, C.; Tiernan, T. O.; Hughes, B. M. *J. Chem. Phys.* **1973**, *59*, 3182–3192. (b) Based on the absence of electron transfer from c-$C_5H_5^-$ (EA(c-$C_5H_5$ = 41.2 ± 0.5 kcal/mol)[29] to $C_6F_6$, EA($C_6F_6$) < 41 kcal/mol was assigned.[28]

[28] McDonald, R. N.; Chowdhury, A. K.; Setser, D. W. *J. Am. Chem. Soc.* **1981**, *103*, 7586–7589.

[29] Engelking, P. C.; Lineberger, W. C. *J. Chem. Phys.* **1977**, *67*, 1412–1417.

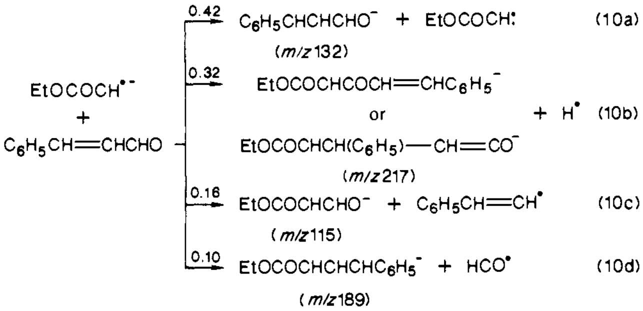
[30] Drazaric, P. S.; Marks, J.; Brauman, J. I. In *Gas Phase Ion Chemistry*; Bowers, M. T., Ed.; Academic Press: New York, 1984; Vol. 3, Chapter 21.

[31] Engelking, P. C.; Ellison, G. B.; Lineberger, W. C. *J. Chem. Phys.* **1978**, *69*, 1826–1832.

[32] Assuming EA($C_2H_5OCOCH_2^{\bullet}$) = EA($CH_3OCOCH_2^{\bullet}$) = 41.5 ± 1.4 kcal/mol.[30]

be favored for the carbon-centered anion radical.

Reaction of $EtOCOCH^{\bullet -}$ with $C_6H_5CH{=}CHCHO$ produced at least four anionic products (reactions 10a–10d). Electron transfer (i.e., a charge exchange reaction) produces the major product. Formation of the anions with $m/z$ 217 and 115 may result from nucleophilic attack at carbonyl carbon with subsequent loss of either $H^{\bullet}$ or $C_6H_5CH{=}CH^{\bullet}$. However, the loss of a hydrogen atom could also occur following radical attack at the $\beta$ carbon generating a radical center of the $\alpha$ carbon, followed by loss of a hydrogen atom (a 1,4-addition process). Observation of the minor product ($m/z$ 189) is somewhat unexpected and may be rationalized as arising from radical attack at the $\alpha$ carbon (a 1,3-addition process) followed by loss of formyl radical.



### Reactions of $EtOCOCH^{\bullet -}$ with $CH_3X$ (X = Cl and Br), $O_2$, $N_2O$, $CO_2$, and $CS_2$

Carboethoxycarbene anion radicals undergo slow and moderate rate $S_N2$ displacement reactions with $CH_3Cl$ and $CH_3Br$, to yield chloride and bromide, respectively, suggesting that $EtOCOCH^{\bullet -}$ is a weak to moderate nucleophile. Although no reaction was observed with $O_2$, $N_2O$, or $CO_2$, $EtOCOCH^{\bullet -}$ reacts rapidly with $CS_2$ via S atom abstraction to yield $EtOCOCHS^-$.

### Summary and Conclusion

In contrast to results from flowing afterglow studies, ethyl diazoacetate produces abundant carboethoxycarbene anion radical ($EtOCOCH^{\bullet -}$) under low-pressure FTMS conditions. Collision-induced dissociation studies suggest that $EtOCOCH^{\bullet -}$ eliminates $C_2H_4$ via a six-membered transition state, yielding $C_2H_2O_2^-$ anion. For the reactions studied, the reactions of carboethoxycarbene anion radical are best understood by considering two resonance structures: I, a carbon-centered radical anion, and II, an oxygen-centered anion. The reactions of $EtOCOCH^{\bullet -}$ with carbonyl compounds and activated olefins are consistent with more carbon-centered anionic character. Competitive $D^+$ transfer, H/D exchange, and D atom abstraction reactions with EtOD support this interpretation. By bracketing proton transfer and H atom abstraction reactions, PA($EtOCOCH^{\bullet -}$) = 377 ± 2 kcal/mol and $D$(EtOCOCH-H) ≥ 101 ± 1 kcal/mol are determined. Using the PA together with other thermochemical data, $\Delta H_f$(EtOCOCH$^{\bullet -}$) is estimated to be −48.5 ± 3 kcal/mol.

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**Registry No.** $EtOCOCHN_2$, 623-73-4; $EtOCOCH^{\bullet -}$, 119638-74-3; H, 1333-74-0.

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# Thermal Stability of the C–O Bond of Methanol on the Pd(111) Surface: An Isotopic Mixing Study

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*Contribution from the Surface Science Center, Department of Chemistry, University of Pittsburgh, Pittsburgh, Pennsylvania 15260.* *Received September 15, 1988*

**Abstract:** The isotopic mixing method was employed to study the thermal desorption of CO molecules produced from methanol decomposition on Pd(111). Using $^{13}CH_3{}^{16}OH$ and $^{12}CH_3{}^{18}OH$ adsorbate molecules, no isotopic exchange in thermally desorbing CO to produce $^{13}C^{18}O$ and $^{12}C^{16}O$ was observed. This observation, combined with measurements indicating that no $H_2O$ or $CH_4$ desorbs, indicates that C–O bond scission does not occur in any of the surface species derived from adsorbed $CH_3OH$.

Can the C–O bond of methanol be thermally dissociated on the Pd(111) surface? In a recent SIMS (secondary ion mass spectroscopy) and XPS (X-ray photoelectron spectroscopy) study,[1] the results were interpreted to indicate efficient C–O bond scission of chemisorbed methanol on Pd(111) at 175 K. This report of the thermal activation of the C–O bond of methanol on the Pd surface differs from current models of $CH_3OH$ interaction with transition-metal surfaces, where decomposition to CO and $H_2$ is postulated to occur via the methoxy intermediate. In order to directly examine the possibility of C–O bond scission, we have performed experiments involving coadsorption of $^{13}CH_3{}^{16}OH$ and $^{12}CH_3{}^{18}OH$ on the Pd(111) surface at various adsorption temperatures from 87 to 265 K. Any isotopic mixing in the desorbing CO products would be indicative of C–O bond breaking and recombination in $CH_3OH$(a), $CH_3O$(a), or CO(a). However, our study shows negative results: no measurable production of $^{13}C^{18}O$ and $^{12}C^{16}O$ is observed compared to the isotope abundance in the labeled methanol adsorbate; no methane or water desorbs within detection limits conservatively estimated to be ~1% of a monolayer based on calibration experiments. Our experimental observations are therefore consistent with other studies on Pd surfaces,[2–6] as well as with the selective methanol formation (with respect to methane) from synthesis gas (CO + $H_2$) on supported Pd catalysts at high pressure.[7–9]

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(1) Levis, R. J.; Jiang, Z.; Winograd, N. *J. Am. Chem. Soc.* **1988**, *110*, 4431.

(2) Lüth, H.; Rubloff, G. W.; Grobman, W. D. *Surf. Sci.* **1977**, *63*, 325.

(3) Christmann, K.; Demuth, J. E. *J. Chem. Phys.* **1982**, *76*, 6308, 6318.

(4) Gates, J. A.; Kesmodel, L. L. *J. Catal.* **1983**, *83*, 437.

(5) Kok, G. A.; Noordermeer, A.; Nieuwenhuys, B. E. *Surf. Sci.* **1983**, *135*, 65.

(6) Davis, J. L.; Barteau, M. A. *Surf. Sci.* **1987**, *187*, 387.

(7) Poutsma, M. L.; Elek, L. F.; Ibarbia, P. A.; Risch, A. P.; Rabo, J. A. *J. Catal.* **1978**, *52*, 157.

(8) Driessen, J. M.; Poels, E. K.; Hindermann, J. P.; Ponec, V. *J. Catal.* **1983**, *82*, 26.

(9) Sudhakar, C.; Vannice, M. A. *J. Catal.* **1985**, *95*, 227.

0002-7863/89/1511-3155$01.50/0