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GENERATION AND ION-MOLECULE REACTIONS OF ETHYL DIAZOACETATE ANION RADICAL ($EtO_2CCHN_2^{\cdot-}$)

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Abstract—Thermal electron attachment to EtO_2CCHN_2 produced the parent anion radical $EtO_2CCHN_2^{\cdot-}$ (m/z 114). The ion–molecule reactions of m/z 114 with 30 neutral substrates were examined. Using the bracketing method, $PA(EtO_2CCHN_2^{\cdot-}) = 355 \pm 4$ kcal mol^{-1} was determined. The reaction of m/z 114 with CH_3SH produced $H_2CS^{\cdot-}$, the product of β-elimination of $H_2^{\cdot+}$ from the thiol. From a series of bracketing studies and determination of the equilibrium constant for the electron transfer (ET) process

$$CH_3C({=}O)C({=}O)CH_3^{\cdot-} + EtO_2CCHN_2 = CH_3C({=}O)C({=}O)CH_3 + EtO_2CCHN_2^{\cdot-}$$

$EA(EtO_2CCHN_2) = 19.7$ kcal mol^{-1} was derived. Both associative and dissociative ET were observed in the reactions of m/z 114 with certain perhalomethanes (depending on their EA) as well as halogen-atom abstraction from $BrCCl_3$. While no reaction was observed between m/z 114 with CH_3CHO or $(CH_3)_2C{=}O$, m/z 114 reacted with certain other ketones and esters (CF_3CO_2R) mainly to yield enolate anions of the β-keto esters, $EtO_2CCH{=}C(O^-)R$. These enolate anions are believed to be formed by nucleophilic addition of C_α of m/z 114 to the carbonyl group of the neutral substrate followed by loss of N_2 and radical β-fragmentation.

Our interest in generating, and determining the thermochemical properties and reactions of hypovalent ion radicals (HIRs) played a major role in our entry into the area of gas-phase ion–molecule chemistry in 1978. Hypovalent ion radical molecules are defined as charged radical species which contain *less* than the number of attached substituents found in the neutral free-radical system normally associated with the central atom of the free radical. Carbene anion radicals ($R_2C^{\cdot-}$) are an anionic (HAR) subclass of carbon-centered HIR molecules which have the electron pair of the anion and the spin-unpaired electron of the radical formally located on the central carbon atom. Thus, $R_2C^{\cdot-}$ is expected to behave chemically as a base and nucleophile, and as a free radical with kinetic and product variations within this subclass of HARs dependent on the nature of the R groups.

The method of generating $R_2C^{\cdot-}$ we have used involves dissociative electron attachment (DEA) with the corresponding diazoalkane (Eq. 1). This method

$$R_2C{=}N_2 + e^- \rightarrow [R_2CN_2^{\cdot-}] \rightarrow R_2C^{\cdot-} + N_2 \quad (1)$$

has proven useful for generation of the carbene anion radicals $c\text{-}C_5H_4^{\cdot-}$,[1] $(CF_3)_2C^{\cdot-}$,[2] $CF_3CH^{\cdot-}$,[3] $Ph_2C^{\cdot-}$,[4] and 9-fluorenylidene$^{\cdot-}$,[5] and the related nitrogen-centered species $PhN^{\cdot-}$[6] (from $PhN_3 + e^-$). The ready loss of N_2 from the isoelectronic diazo and azide structures on attachment of low energy electrons suggested that this method of generating carbene and nitrene anion radicals was reasonably general.

Two earlier results, however, illustrate different limitations to this method. First, DEA with t-butoxycarbonyl azide serves as an excellent and clean source of N_3^- (Eq. 2), but does *not* yield the nitrene anion radical $(CH_3)_3CO_2CN^{\cdot-}$. The second result involved

$$(CH_3)_3COC({=}O)N_3 + e^- \rightarrow N_3^- + (CH_3)_3COC({=}O). \quad (2)$$

DEA with diethyl diazomalonate (**1**). In the condensed phase, electrochemical reduction of **1** yields the carbene anion radical $(EtO_2C)_2C^{\cdot-}$ via intermediate formation of the diazo ester anion radical.[7] In the gas phase, we observe that **1** undergoes DEA yielding the anion m/z 186 (Eq. 3) which is, most likely, the

$$\underset{\mathbf{1}}{(EtO_2C)_2C{=}N_2} + e^- \xrightarrow[-N_2]{} [(EtO_2C)_2C^{\cdot-}]^*$$

$$\rightarrow \underset{(m/z\ 186)}{EtO_2C{-}\bar{C}{=}C{=}O} + {\cdot}OEt \quad (3)$$

carboethoxyketenyl anion, the result of radical β-fragmentation (loss of ·OEt) from the vibrationally excited carbene anion radical. These results illustrate the points that:

(a) we must beware of other primary channels than simple loss of N_2, especially with organic azides, and
(b) secondary reaction channels can become important and destroy the desired HAR species.

The present study centers on a further limitation to the generality of Eq. (1), that of failure to lose N_2 from the intermediate diazo anion radical. This possibility will depend on the electron affinity of the diazo alkane and the stability of the resultant carbene anion radical. We have observed that simple electron attachment occurs with two diazo compounds in our pressure regime, $EtO_2CCH{=}N_2$ and $PhCH{=}N_2$, yielding the corresponding diazo alkane anion radicals $RCHN_2^{\cdot-}$ ($R = EtO_2C$ and Ph). Our interest in the thermochemical properties and chemistry of diazo alkane anion radicals stems from the fact that these reduced species are the principal or exclusive reactive intermediates formed in the electroreduction of diazoalkanes in the condensed phase.[7] Thus, our ability to cleanly generate and determine the reactions of diazoalkane anion radicals in the gas phase should yield more information about their thermochemical

Table 1. Summary of kinetic and primary product data for the ion–molecule reactions of $EtO_2CCHN_2^{\cdot -}$ (*m/z* 114) with various neutral substrates

Reaction No.	Ion + Neutral Reactants	→ Products [Assumed Neutral]	Fraction of product ion signal	K_{total}[a] (cm^3 molecule^{-1} s^{-1})	k_{ADO}[b] (cm^3 molecule^{-1} s^{-1})
1	$EtO_2CCHN_2^{\cdot -} + HCO_2H$	$\rightarrow HCO_2^-[+EtO_2CCH_2N_2\cdot]$	1.00	fast[c]	
2	$EtO_2CCHN_2^{\cdot -} + (CF_3)_2CHOH$	$\rightarrow (CF_3)_2CHO^-[+EtO_2CCH_2N_2\cdot]$	1.00	fast[c]	
3	$EtO_2CCHN_2^{\cdot -} + PhOH$	$\rightarrow PhO^-[+EtO_2CCH_2N_2\cdot]$	1.00		
4	$EtO_2CCHN_2^{\cdot -} + H_2S$	$\rightarrow HS^-[+EtO_2CCH_2N_2\cdot]$	1.00	3.6×10^{-10}	1.2×10^{-9}
5	$EtO_2CCHN_2^{\cdot -} + c\text{-}C_3H_6$	→ no reaction		$< 10^{-13}$	
6	$EtO_2CCHN_2^{\cdot -} + CH_3NO_2$	$\xrightarrow{He} EtO_2CCHN_2^{\cdot -}/CH_3NO_2$	1.00	1.0×10^{-12e}	
7	$EtO_2CCHN_2^{\cdot -} + HOCH_2CF_3$	$\xrightarrow{He} EtO_2CCHN_2^{\cdot -}/HOCH_2CF_3$	1.00		
8	$EtO_2CCHN_2^{\cdot -} + HCCl_3$	$\xrightarrow{He} EtO_2CCHN_2^{\cdot -}/HCCl_3$	1.00	$\sim 2.0 \times 10^{-13e}$	
9	$EtO_2CCHN_2^{\cdot -} + CH_3SH$	$\rightarrow H_2CS^{\cdot -}[+CH_3CO_2Et+N_2]$	1.00	3.6×10^{-11}	
10a	$EtO_2CCHN_2^{\cdot -} + ICF_3$	$\rightarrow I^-[+\cdot CF_3+EtO_2CCHN_2]$	0.97	5.6×10^{-10}	1.2×10^{-9}
10b		$\rightarrow ICF_3^{\cdot -}[+EtO_2CCHN_2]$	0.03		
11	$EtO_2CCHN_2^{\cdot -} + BrCF_3$	$\rightarrow Br^-[+\cdot CF_3+EtO_2CCHN_2]$	1.00		
12	$EtO_2CCHN_2^{\cdot -} + ClCF_3$	→ no reaction		$< 10^{-13}$	
13a	$EtO_2CCHN_2^{\cdot -} + BrCCl_3$	$\rightarrow Br^-[+\cdot CCl_3+EtO_2CCHN_2]$	0.53	3.8×10^{-10}	9.3×10^{-10d}
13b		$\rightarrow Cl^-[+\cdot CBrCl_2+EtO_2CCHN_2]$	0.03		
13c		$\rightarrow Cl^-/EtO_2CCHN_2[+\cdot CBrCl_2]$	0.19		
13d		$\rightarrow Cl_3C^-[+EtO_2CCHBrN_2\cdot]$	0.13		
13e		$\rightarrow Cl_2CBr^-[+EtO_2CHClN_2\cdot]$	0.12		
14a	$EtO_2CCHN_2^{\cdot -} + CCl_4$	$\rightarrow Cl^-[+\cdot CCl_3+EtO_2CCHN_2]$	variable		
14b		$\rightarrow Cl^-/EtO_2CCHN_2[+\cdot CCl_3]$	variable		
15	$EtO_2CCHN_2^{\cdot -} + CH_3I$	$\rightarrow I^-$ [see text]	1.00	$\sim 1.0 \times 10^{-13}$	

16	$EtO_2CCHN_2^{\cdot -} + CH_3Br$	→ no reaction		$<10^{-13}$	
17	$EtO_2CCHN_2^{\cdot -} + CH_3CHO$	→ no reaction		$<10^{-13}$	
18	$EtO_2CCHN_2^{\cdot -} + (CH_3)_2C{=}O$	→ no reaction		$<10^{-13}$	
19a	$EtO_2CCHN_2^{\cdot -} + CH_3C({=}O)C({=}O)CH_3$	$\rightarrow EtO_2CCH{=}C(O^-)CH_3[+CH_3CO\cdot + N_2]$	0.77	2.4×10^{-11}	9.5×10^{-10}
19b		$\rightarrow CH_3C({=}O)C({=}O)CH_3^{\cdot -}[+EtO_2CCHN_2]$	0.23		
20a	$EtO_2CCHN_2^{\cdot -} + (CF_3)_2C{=}O$	$\rightarrow EtO_2CCH{=}C(O^-)CF_3[+\cdot CF_3 + N_2]$	0.25	4.7×10^{-10}	1.1×10^{-9}
20b		$\rightarrow (CF_3)_2CO^{\cdot -}[+EtO_2CCHN_2]$	0.75		
21a	$EtO_2CCHN_2^{\cdot -} + CF_3C({=}O)CH_3$	$\rightarrow EtO_2CCH{=}C(O^-)CH_3[+\cdot CF_3 + N_2]$	0.61	1.0×10^{-10}	9.8×10^{-10}[d]
21b		$\rightarrow EtO_2CCH{=}C(O^-)CF_3[+\cdot CH_3 + N_2]$	0.25		
21c		→ *m/z* 207 [+·F]	0.10		
21d		→ *m/z* 206 [+HF]	0.04		
22	$EtO_2CCHN_2^{\cdot -} + CF_3CO_2CH_3$	$\rightarrow EtO_2CCH{=}C(O^-)CF_3[+\cdot OCH_3 + N_2]$	1.00	8.4×10^{-12}	1.5×10^{-9}
23	$EtO_2CCHN_2^{\cdot -} + CF_3CO_2C_2H_5$	$\rightarrow EtO_2CCH{=}C(O^-)CF_3[+\cdot OC_2H_5 + N_2]$	1.00	7.8×10^{-12}	1.5×10^{-9}
24a	$EtO_2CCHN_2^{\cdot -} + NO_2$	$\rightarrow NO_2^-[+EtO_2CCHN_2]$	0.94	4.4×10^{-10}	6.7×10^{-10}
24b		$\xrightarrow{He} NO_2^-/EtO_2CCHN_2$	0.04		
25	$EtO_2CCHN_2^{\cdot -} + SO_2$	$\rightarrow SO_2^{\cdot -}[+EtO_2CCHN_2]$	1.00	1.3×10^{-9}	1.2×10^{-9}
26	$EtO_2CCHN_2^{\cdot -} + Fe(CO)_5$	$\rightarrow [OC)_4Fe^{\cdot -}[+CO + EtO_2CCHN_2]$	1.00		
27	$EtO_2CCHN_2^{\cdot -} + c\text{-}C_5H_4{=}N_2$	$\rightarrow c\text{-}C_5H_4N_2^{\cdot -}[+EtO_2CCHN_2]$	1.00		
28	$EtO_2CCHN_2^{\cdot -} + SF_6$	→ no reaction		$<10^{-13}$	
29	$EtO_2CCHN_2^{\cdot -} + PhN_3$	→ no reaction		$<10^{-13}$	
30	$EtO_2CCHN_2^{\cdot -} + C_6F_6$	→ no reaction		$<10^{-13}$	

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[a] *k*'s are estimated to be accurate to ±25%. No P_{He} dependency was observed on *k*'s or the branching fractions when P_{He} was varied from 0.4 to 1.1 Torr.

[b] Collision limited *k*'s are calculated by the average dipole orientation theory (T. Su and M. T. Bowers, *Gas Phase Ion Chemistry* (Edited by M. T. Bowers), Vol. 1, Chap. 3. Academic Press, New York (1979)).

[c] Although the rate of this reaction was not measured, it was judged to have $k > 10^{-10}$ cm^3 molecule^{-1} s^{-1}.

[d] Calculated using Langevin theory.

[e] The apparent bimolecular rate constant for this termolecular reaction is given.

properties and chemistry than is presently possible in the condensed phase. In this study, we will deal with a variety of reactions observed with $EtO_2CCHN_2^{\cdot-}$.

EXPERIMENTAL

The flowing afterglow (FA) apparatus (Fig. 1) with the modular flow tube used in these investigations has been previously described.[1,8] Briefly, a small amount of EtO_2CCHN_2 is continuously added to a fast flow of helium buffer gas ($P_{He} = 0.5$ Torr, $\bar{v} = 80$ m s^{-1}, 298 K) via an inlet port located just downstream of the electron gun. The diazo ester attaches thermal or near-thermal electrons producing a constant ion signal of $EtO_2CCHN_2^{\cdot-}$ (*m/z* 114). Excess vibrational energy in *m/z* 114 is removed by multiple collisions with the buffer gas in the next 35 cm of the flow tube. No signals for $SF_6^{\cdot-}$ or $SF_5^{\cdot-}$ were observed by addition of SF_6 via an inlet located 10 cm downstream of the inlet port through which EtO_2CCHN_2 was added. This demonstrated that all available electrons were attached and that *m/z* 114 was not formed in the flow tube beyond this point.

Following thermalization of the *m/z* 114 ions in the fast helium flow, neutral reactant molecules can then be added via a gas inlet port and the reactions of *m/z* 114 with these reactants then occur in the final 65 cm of the flow tube. The fast gas flow is established and maintained for the duration of the experiment by a large, fast pumping system. The flow is sampled at the end of the flow tube into a differentially pumped compartment containing a quadrupole mass filter and electron multiplier which continuously monitor the ion composition of the gas flow. The structures of neutral products of the ion–molecule reaction are assumed based on thermochemistry and mass balance since they are not directly observed.

Kinetics of the ion–molecule reactions of *m/z* 114 with added neutral substrates, N, are determined under pseudo-first-order conditions where the concentration of [N] is in large excess over that of the ion concentration. We maintain the *m/z* 114 ion generation and the 65 cm reaction distance as constants, and vary the concentration of [N]; at each new concentration of added substrate, the signal intensities of *m/z* 114 and that of the product ion(s) are measured. From a plot of log *m/z* 114 signal vs increasing concentration of [N] added to the flow, the resulting linear decay of *m/z* 114 is then transformed into the bimolecular rate constant by equations already given.[1]

The helium used in this study was of 99.99% purity supplied by Welders Products (Topeka, Kansas, USA) and was further purified by passage through two traps filled with Davison 4-Å molecular sieves cooled with liquid nitrogen and then warmed to room temperature in a glass coil prior to introduction to the flow tube. Gas and liquid neutral reagents were obtained from standard commercial sources. The liquid reagents were distilled just prior to use and a center-cut, constant-boiling-point sample was transferred to a gas storage bulb after three freeze–pump–thaw degassing cycles. The gas reagents were used directly.

Ethyl diazoacetate was prepared according to a literature method.[9] The purified ester was subjected to three freeze–pump–thaw degassing cycles and kept in a liquid storage flask (15 ml) with a gas metering valve, an on–off valve, and an O-ring joint to allow connection of the flask to an O-ring joint at inlet 1 (Fig. 1). Although no difficulties were encountered with this diazo ester in these experiments, *CAUTION* should always be exercised in the handling of this and related diazo reagents.

RESULTS

General considerations. The kinetic and primary product data for the ion–molecule reactions of $EtO_2CCHN_2^{\cdot-}$ (*m/z* 114) are summarized in Table 1. In all cases, clean pseudo-first-order decay plots of the log *m/z* 114 signal vs concentration of the neutral reactants were observed. The primary product ion distributions in Table 1 are the relative integrated ion signals observed from the series of negative ion mass spectra taken at varying concentrations of a specific neutral reactant; "variable" means that fast secondary ion–molecule reactions are encountered which obscure the primary product ion composition.

Reactions of $EtO_2CCHN_2^{\cdot-}$ *with potential proton donors*

To determine the proton affinity (PA) of $EtO_2CCHN_2^{\cdot-}$, we examined the reactions of *m/z* 114 with a series of potential proton donor molecules of known gas-phase acidity[10] (entries 1–9, Table 1). Excluding the results with CH_3SH (entry 9, Table 1), the data pertaining to H^+-transfer are given in Table 2 in the decreasing order of gas-phase acidity of the HA molecules; ΔH°_{acid} is the enthalpy change for the heterolytic cleavage $HA = A^- + H^+$.[10]

Two transitions of H^+-transfer to *no* H^+-transfer are observed in the series of potential H^+-donors in Table 2. One occurs between C_6H_5OH and $CF_3C({=}O)CH_3$, the second between H_2S and c-C_5H_6. The absence of H^+-transfer from the carbon acid $CF_3C({=}O)CH_3$ can be accounted for by the presence of other product forming channels (discussed later) being faster than that of H^+-transfer. This is not without precedence since H^+-transfer from many carbon acids have been shown to be slow.[11]

H^+-Transfer was observed between $EtO_2CCHN_2^{\cdot-}$ and H_2S as judged by attenuation of the *m/z* 114 signal and formation of HS^- (*m/z* 33). When cyclopentadiene was introduced to the fast helium flow containing *m/z* 114, neither attenuation of the *m/z* 114 signal or formation of any new signal between 4–280 amu was observed; therefore, $k < 10^{-13}$ cm^3 molecule^{-1} s^{-1}. To confirm that this is the lower end of the bracket for PA($EtO_2CCHN_2^{\cdot-}$), the slow reaction of *m/z* 114 with CH_3NO_2 was observed to yield only the cluster ion at *m/z* 175, considered to be the hydrogen bonded complex $EtO_2CCHN_2^{\cdot-}/CH_3NO_2$; if H^+-transfer between *m/z* 114 and CH_3NO_2 had been exothermic or thermoneutral, it should have been observed by formation of $O_2NCH_2^-$ or its cluster ion $O_2NCH_2^-/CH_3NO_2$.

The reaction of $EtO_2CCHN_2^{\cdot-}$ with CF_3CH_2OH is interesting in that it involves a cluster-to-cluster transformation in an anion-switching mechanism[12] shown in Eq. (4). The primary step in this reaction is

$$\begin{tikzcd}
\underset{(m/z\ 114)}{EtO_2CCHN_2^{\cdot-}} + HOCH_2CF_3 \arrow[r] & \underset{(m/z\ 214)}{EtO_2CCHN_2^{\cdot-}/HOCH_2CF_3} \arrow[d, "CF_3CH_2OH"] \\
\underset{(m/z\ 199)}{CF_3CH_2O^-/HOCH_2CF_3} + EtO_2CCH_2N_2^{\cdot} & \underset{2}{[EtO_2CCHN_2^{\cdot-}/(HOCH_2CF_3)_2]} \arrow[l]
\end{tikzcd}$$

(4)

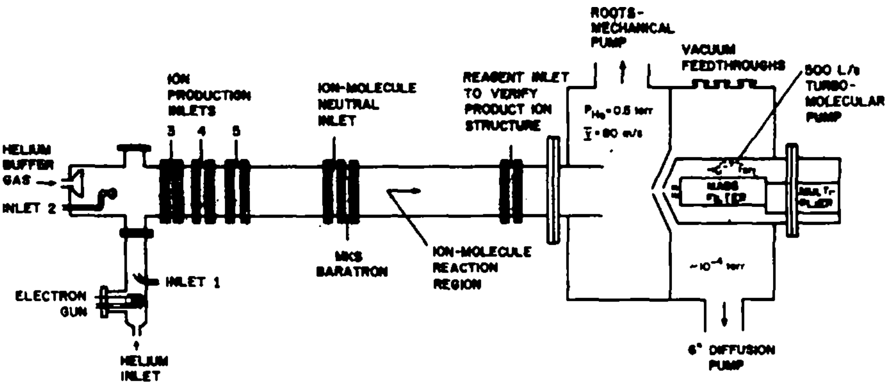

Fig. 1. Schematic diagram of the flowing afterglow apparatus.

Table 2. Reaction of $EtO_2CCHN_2^{\cdot -}$ with potential proton donors used to bracket PA($EtO_2CCHN_2^{\cdot -}$)

HA	H^+-Transfer[a]	ΔH°_{acid} (HA) = PA(A^-)[b] (kcal mol^{-1})
HCO_2H	yes	345.2±2
$(CF_3)_2CHOH$	yes	348.4±2
C_6H_5OH	yes	349.8±2
$CF_3C(=O)CH_3$	no[c]	350.3±2
H_2S	yes	353.4±2
c-C_5H_6	no[d]	356.1±2
CH_3NO_2	no[e]	358.7±2
CF_3CH_2OH	no[e]	364.4±2
$HCCl_3$	no[e]	362±6

[a] Proton transfer is judged to have occurred by attenuation of the signal of m/z 114 *and* formation of the signal for A^-.

[b] Ref. 10.

[c] Four addition product channels were observed with this neutral.

[d] No reaction was observed; $k < 10^{-13}$ cm^3 $molecule^{-1}$ s^{-1}.

[e] Adduct formation (m/z 114/HA) was observed with this HA molecule.

formation of the hydrogen bonded cluster ion m/z 214. The signal intensity of m/z 214 goes through an early maximum in the plot of log ion signal vs increasing concentration of CF_3CH_2OH added to the flow and then decays as the secondary reaction of m/z 214 with CF_3CH_2OH yields the alkoxide–alcohol cluster m/z 199. Further clustering occurs with m/z 199 and additional CF_3CH_2OH yielding $CF_3CH_2O^-/(HOCH_2CF_3)_2$ (m/z 299). H^+-Transfer between $EtO_2CCHN_2^{\cdot -}$ and a single molecule of CF_3CH_2OH is endothermic, and, thus, cannot be observed under these reaction conditions. However, H^+-transfer to m/z 114 from the alcohol dimer in **2** will be exothermic because of the large binding enthalpy in the homoconjugate cluster ion m/z 199 ($D(CF_3CH_2O^-/HOCH_2CF_3) \sim 24$ kcal mol^{-1}).[12] This result further supports the above conclusion that PA($EtO_2CCHN_2^{\cdot -}$) = 355±4 kcal mol^{-1}, the bracket established with H_2S and c-C_5H_6 as the upper and lower limits, respectively.

A very slow clustering of $EtO_2CCHN_2^{\cdot -}$ with $HCCl_3$ (reaction 8, Table 1) was also observed.

Reaction of $EtO_2CCHN_2^{\cdot -}$ *with* CH_3SH

The reaction of $EtO_2CCHN_2^{\cdot -}$ with CH_3SH was studied from the simple approach of using CH_3SH as a potential proton donor ($\Delta H^\circ_{acid} = 359.0 \pm 2$ kcal mol^{-1}).[10] Although formation of the conjugate base CH_3S^- was observed, it was clearly formed in a secondary ion–molecule reaction. The primary process was formation of the negative ion m/z 46 with isotope signals at m/z 47 ((M+1); ~1%) and 48 ((M+2); 4%) which establish the presence of one C and one S in this anion;† the remaining 2 amu must then be two Hs. We assign the structure of this negative ion as the thioformaldehyde anion radical, $H_2CS^{\cdot -}$.‡ The overall transformation of CH_3SH to $H_2CS^{\cdot -}$ requires the β-elimination of H_2^+ from the thiol (Eq. 5) *in a single collision encounter with* $EtO_2CCHN_2^{\cdot -}$.§ The secondary reaction of $H_2CS^{\cdot -}$ with CH_3SH giving CH_3S^- (Eq. 6) proceeds by either H^+ or H-atom abstraction

$$\underset{(m/z\ 114)}{EtO_2CCHN_2^{\cdot -}} + CH_3SH \rightarrow \underset{(m/z\ 46)}{H_2CS^{\cdot -}} + \underset{\mathbf{3}}{(EtO_2CCHN_2^{\cdot -} + H_2^+)} \quad (5)$$

$$\underset{(m/z\ 46)}{H_2CS^{\cdot -}} + CH_3SH \rightarrow \underset{(m/z\ 47)}{CH_3S^-} + CH_3S. \quad (6)$$

Several possibilities exist for the structure of the neutral product **3** formed in Eq. (5). Two structures would be the hydrazone $EtO_2CCH{=}NNH_2$ (H_2^+ addition to N_β of m/z 114) and the diazine $EtO_2CCH_2N{=}NH$ (1,3-addition of H_2^+ to m/z 114).

A third possibility is that the neutral product is the result of fragmentation yielding $CH_3CO_2Et + N_2$. This method of generating the neutral product may be the result of the low S—H bond energy ($D(CH_3S{-}H) = 91.8 \pm 2$ kcal mol^{-1})[15] and relatively high acidity. While the source of the H-atom and of the H^+(C—H or SH) from CH_3SH

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† Measurement of the isotope signals was accomplished at low concentrations of added CH_3SH, so that the H^+-transfer (Eq. 6) was not yet important.

‡ While the electron affinities (EAs) of simple carbonyl containing molecules, e.g. H_2CO, CH_3CHO, and $(CH_3)C{=}O$, are negative,[13] Professor Burrows (private communication) informs us that the corresponding thiocarbonyl derivatives should have significant positive EAs.

§ Formation of $H_2CS^{\cdot -}$ (m/z 46) has also been observed in the ion–molecule reaction of $CF_3CH^{\cdot -} + CH_3SH$.[14]

are unknown, the most likely intermediates to undergo the necessary fragmentation reaction (loss of N_2) are $EtO_2CCH_2N_2^{\cdot}$ ($\rightarrow EtO_2CCH_2^{\cdot}+N_2$) or $EtO_2CCH_2N_2^-$ ($\rightarrow EtO_2CCH_2^-+N_2$). H^+-Transfer between $EtO_2CCHN_2^{\cdot-}$ and CH_3SH is endothermic by 4 kcal mol^{-1} and could only occur in the excited collision complex $[EtO_2CCHN_2^{\cdot-}/HSCH_3]^*$ which would be stabilized by ion-dipole and ion-induced dipole forces with a potential energy well depth of 10–20 kcal mol^{-1}. If this is the mechanism operating here, $D(EtO_2CCH_2{-}H)$† must then be greater than $D(^-SCH_2{-}H)$ to complete the sequence. Related arguments apply if the sequence proceeds via initial H-atom transfer followed by H^+-transfer. We favor this explanation, but the first two possibilities considered above cannot be ruled out.

Reactions of $EtO_2CCHN_2^{\cdot-}$ *with certain halomethanes*

The reaction of *m/z* 114 with ICF_3 (EA = 1.57 ± 0.2 eV)[17] produced mainly I^- along with 3% $ICF_3^{\cdot-}$ (Eq. 7). Formation of these two product ions and their

$$\begin{array}{c}
I^- + {}^{\cdot}CF_3 \\
(m/z\ 127) \\
{\scriptstyle (0.97)}\uparrow \\
EtO_2CCHN_2^{\cdot-} + ICF_3 \rightarrow [ICF_3^{\cdot-}]^* + EtO_2CCHN_2 \\
{\scriptstyle (0.03)}\downarrow{\scriptstyle He} \\
ICF_3^{\cdot-} \\
(m/z\ 196)
\end{array} \qquad (7)$$

distribution is that expected for an exothermic electron transfer to ICF_3 by $EtO_2CCHN_2^{\cdot-}$.

The reaction of $EtO_2CCHN_2^{\cdot-}$ with $BrCF_3$ (EA = 0.91 ± 0.2 eV)[17] was very slow (reaction 11, Table 1), and yielded Br^- (major) and a minor amount of an apparent ion–dipole complex $Br^-/BrCF_3$ (*m/z* 227, 229, 231). However, we were surprised to find that the sum of these negative ion products accounted for only ~25% of the $EtO_2CCHN_2^{\cdot-}$ ion signal decayed by the addition of $BrCF_3$. That this "loss" of product ion signal was not the result of electron detachment was shown by the absence of formation of $SF_6^{\cdot-}$ when SF_6 was added to the flow containing *m/z* 114 prior to addition of $BrCF_3$. As previously pointed out in the Experimental, $EtO_2CCHN_2^{\cdot-}$ does not electron transfer to SF_6.

No reaction was observed between *m/z* 114 and $ClCF_3$.

The fast reaction of $EtO_2CCHN_2^{\cdot-}$ with $BrCCl_3$ (reaction 13, Table 1) produced Br^-, Cl^-, Cl^-/EtO_2CCHN_2, Cl_3C^-, and Cl_2CBr^- in the distribution shown in Eq. (8). In our FA experiments, attachment of thermal and near-thermalized electrons to $BrCCl_3$ is dissociative yielding a mixture of Br^- (94%) and Cl^- (6%). In separate experiments, Cl^- was shown to form an adduct with EtO_2CCHN_2, but Br^- did not react with the neutral diazo ester. Formation of Cl_3C^- cannot be the result of dissociation of $[BrCCl_3^{\cdot-}]^*$ because of the lower EA of $Cl_3C^{\cdot}$ (1.43 eV)[18] compared to those of $Cl^{\cdot}$ (3.615 eV)[20] and $Br^{\cdot}$ (3.364 eV).[19]

$$EtO_2CCHN_2^{\cdot-} + BrCCl_3 \left\{\begin{array}{ll}
\xrightarrow{(0.53)} Br^- & (8a)\\
\xrightarrow{(0.22)} Cl^- + Cl^-/EtO_2CCHN_2 & (8b)\\
\xrightarrow{(0.13)} Cl_3C^- & (8c)\\
\xrightarrow{(0.12)} Cl_2CBr^- & (8d)
\end{array}\right.$$

The ratio of Br^-/Cl^- (95/5) formed in reaction 13, Table 1 (Eq. 8) is that observed from dissociative electron attachment to $BrCCl_3$. The additional 19% of Cl^-/EtO_2CCHN_2 is believed to be derived by selective interaction of the diazo ester with C—Cl bonds in the excited collision complex $[(BrCCl_3/EtO_2CCHN_2)^{\cdot-}]^*$. The other two product ions, Cl_3C^- and Cl_2CBr^-, appear to arise by Br- and Cl-atom abstraction, respectively, from $BrCCl_3$ in the collision complex. This explanation requires that atom abstraction and electron transfer, the latter most probably being endothermic, are competitive in the vibrationally excited collision complex.

The reaction of diazo ester anion radical *m/z* 114 with CCl_4 proceeded exclusively by dissociative electron transfer and produced the negative ions Cl^- (*m/z* 35, 37) and the cluster Cl^-/EtO_2CCHN_2 (*m/z* 149, 151). The majority of the cluster ion *m/z* 149, 151 is believed to be formed by association of the neutral diazo ester to Cl^- generated in the dissociating, transient collision complex $[CCl_4^{\cdot-}/EtO_2CCHN_2]^*$.

No reaction was observed between $EtO_2CCHN_2^{\cdot-}$ and CH_3Br. The very slow reaction of *m/z* 114 with CH_3I yielding I^- was just measurable at the lower limit of our FA experiments. It is not possible to tell whether this is the result of S_N2 displacement or dissociative electron transfer (EA(CH_3I) = 0.2 ± 0.1 eV).[20]

Reactions of $EtO_2CCHN_2^{\cdot-}$ *with carbonyl containing molecules*

Aldehydes and ketones. No reaction was observed between $EtO_2CCHN_2^{\cdot-}$ and CH_3CHO or $(CH_3)_2C{=}O$. Reaction of *m/z* 114 with the α-diketone biacetyl (reaction 19, Table 1) occurred with a modest rate constant and produced two primary product negative ions *m/z* 129 and 86 (Eq. 9). Ion *m/z* 129 is considered to be the stable enolate anion of ethyl acetoacetate formed by addition of C_α of *m/z* 114 to a carbonyl group of biacetyl followed by loss of N_2 and radical β-fragmentation of the acetyl radical. The ion radical *m/z* 86 has two possible isomeric structures:

(a) the carbene anion radical $EtO_2CCH^{\cdot-}$ or
(b) the biacetyl anion radical.

The structure $EtO_2CCH^{\cdot-}$ is ruled out in this case since the carbene anion radical would be expected to react rapidly with neutral biacetyl and produce the enolate anion *m/z* 129 and/or H^+-transfer, and thus,

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† $D(EtO_2CCH_2{-}H)$ should be approximately that of acetone, $D(CH_3C({=}O)CH_2{-}H) \approx 98.0\pm2.6$ kcal mol^{-1}.[16]

$$\underset{(m/z\ 114)}{EtO_2CCHN_2^{\cdot-}} + (CH_3C({=}O))_2 \xrightarrow{(0.77)} \underset{(m/z\ 129)}{EtO_2CCH{=}C(O^-)CH_3} + N_2 + CH_3CO^{\cdot} \tag{9a}$$

$$\xrightarrow{(0.23)} \underset{(m/z\ 86)}{CH_3C({=}O)C({=}O)CH_3^{\cdot-}} + EtO_2CCHN_2 \tag{9b}$$

would not be observed.† On the other hand, the biacetyl anion radical is a long-lived species readily formed by electron attachment to biacetyl (EA = 16.7 kcal mol^{-1})[22] in our FA.

The fast reaction of anion-radical m/z 114 with $(CF_3)_2C{=}O$ (reaction 20, Table 1) occurred by the two mechanisms outlined with biacetyl, but with an inverted branching fraction (Eq. 10). The greater amount of electron transfer in this reaction yielding $(CF_3)_2CO^{\cdot-}$ compared to that with biacetyl is reasonable because EA($(CF_3)_2CO$) ~ 35 kcal mol^{-1}‡ is approximately twice that of biacetyl. In fact, it may be considered rather remarkable that any of the product channel (10a) forming enolate m/z 183 is observed with the exothermic electron transfer channel (10b), $\delta EA \geqslant 18$ kcal mol^{-1}.

$$\underset{(m/z\ 114)}{EtO_2CCHN_2^{\cdot-}} + (CF_3)_2C{=}O \xrightarrow{(0.25)} \underset{(m/z\ 183)}{EtO_2CCH{=}C(O^-)CF_3} + N_2 + {}^{\cdot}CF_3 \tag{10a}$$

$$\xrightarrow{(0.75)} \underset{(m/z\ 166)}{(CF_3)_2CO^{\cdot-}} + EtO_2CCHN_2 \tag{10b}$$

The reaction of $EtO_2CCHN_2^{\cdot-}$ with $CF_3C({=}O)CH_3$ (reaction 21, Table 1) occurred at a rate slower than that observed with $(CF_3)_2C{=}O$. The major products (Eqs 11a and 11b) were the enolate anions $EtO_2CCH{=}C(O^-)CH_3$ (m/z 129) and $EtO_2CCH{=}C(O^-)CF_3$ (m/z 183) considered to be formed by addition/fragmentation mechanisms similar to those involved in producing these enolate anions in the above reactions of m/z 114 with biacetyl and $(CF_3)_2C{=}O$ in Eqs (9a) and (10a).

$$\underset{(m/z\ 114)}{EtO_2CCHN_2^{\cdot-}} + CF_3C({=}O)CH_3 \xrightarrow{(0.61)} \underset{(m/z\ 129)}{EtO_2CCH{=}C(O^-)CH_3} + N_2 + {}^{\cdot}CF_3 \tag{11a}$$

$$\xrightarrow{(0.25)} \underset{(m/z\ 183)}{EtO_2CCH{=}C(O^-)CF_3} + N_2 + {}^{\cdot}CH_3 \tag{11b}$$

$$\xrightarrow{(0.10)} m/z\ 207 + {}^{\cdot}F \tag{11c}$$

$$\xrightarrow{(0.04)} m/z\ 206 + HF \tag{11d}$$

However, two unusual minor product ions were also formed, m/z 207 (adduct $-{}^{\cdot}F$) and 206 (adduct $-HF$). Both of these product ions incorporate the N_2 entity. The structures of m/z 206 and 207 are unknown as, of course, are the mechanisms by which they are formed; it seems probable that N_β of $EtO_2CC_\alpha HN_\alpha N_\beta^{\cdot-}$ originally binds to carbon or oxygen of the carbonyl group of this ketone competitive with C_α binding to the carbonyl-carbon which leads to m/z 129 and 183.

Esters of CF_3CO_2H. The slow reactions of $EtO_2CCHN_2^{\cdot-}$ with CF_3CO_2R where R = CH_3 and C_2H_5 (reactions 22 and 23, Table 1) produced the same product enolate anion $EtO_2CCH{=}C(O^-)CF_3$ exclusively (Eq. 12). Reactions of m/z 114 with other esters (e.g. HCO_2CH_3 and $CH_3CO_2CH_3$) were not investigated due to the slow rates observed with CF_3CO_2R, and since no measurable reactions were observed with the more reactive carbonyl compounds CH_3CHO and $(CH_3)_2C{=}O$.[21]

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† McDonald and Chowdhury[21] showed that $PhN^{\cdot-}$ reacted with biacetyl at 64% of the collision limit producing 98% $PhN{=}C(O^-)CH_3$, the addition/fragmentation product, and 2% $CH_2{=}C(O^-)C({=}O)CH_3$, the product of H^+-transfer. Other results in McDonald's group establish that the carbene anion radicals $Ph_2C^{\cdot-}$,[4] $(CF_3)_2C^{\cdot-}$,[3] and $CF_3CH^{\cdot-}$[3,5] react rapidly with biacetyl by the addition/fragmentation and/or H^+-transfer mechanisms.

‡ McDonald and Chowdhury[21] observed minor formation of $(CF_3)_2CO^{\cdot-}$ in the reaction of $PhN^{\cdot-}$ with $(CF_3)_2C{=}O$; EA(PhN) = 33.7 kcal mol^{-1}.[23]

$$EtO_2CCHN_2^{\cdot -} + CF_3CO_2R \;(m/z\ 114) \rightarrow EtO_2CCH{=}C(O^-)CF_3 + N_2 + {}^{\cdot}OR \;(m/z\ 183) \quad (12)$$

Reactions of $EtO_2CCHN_2^{\cdot -}$ *with other neutral molecules*

$EtO_2CCHN_2^{\cdot -}$ reacted with NO_2 (EA = 53.3 kcal mol^{-1})[22] by electron transfer forming NO_2^-/EtO_2CCHN_2 (Eq. 13). The cluster ion is probably the hydrogen bonded structure involving the modestly acidic C_α—H of the neutral diazo compound.

$$EtO_2CCHN_2^{\cdot -} + NO_2 \;(m/z\ 114) \begin{cases} \xrightarrow{(0.94)} NO_2^- + EtO_2CCHN_2 \;(m/z\ 46) \\ \xrightarrow[(0.04)]{He} NO_2^-/EtO_2CCHN_2 \end{cases} \quad (13)$$

The fast reaction between $EtO_2CCHN_2^{\cdot -}$ and SO_2 (reactions 25, Table 1) formed $SO_2^{\cdot -}$ (m/z 64), the product of electron transfer, and a substitution product $EtO_2CCHSO_2^{\cdot -}$ (m/z 150) (Eq. 14). Formation of m/z 150 is the result of the ion molecule reaction of $SO_2^{\cdot -}$ with EtO_2CCHN_2. The data suggest that the primary product forming channel in Eq. (14) is electron transfer (Eq. 14a) followed by the secondary ion–molecule reaction in Eq. (15) forming m/z 150.

$$EtO_2CCHN_2^{\cdot -} + SO_2 \rightarrow (EtO_2CCHN_2/SO_2^{\cdot -}) \begin{cases} \rightarrow SO_2^{\cdot -} + EtO_2CCHN_2 \;(m/z\ 64) & (14a) \\ \rightarrow EtO_2CCHSO_2^{\cdot -} + N_2 \;(m/z\ 150) & (14b) \end{cases}$$

$$SO_2^{\cdot -} + EtO_2CCHN_2 \rightarrow EtO_2CCHSO_2^{\cdot -} + N_2 \quad (15)$$
$$(m/z\ 64) \qquad\qquad (m/z\ 150)$$

The reaction of m/z 114 with $Fe(CO)_5$ (reaction 26, Table 1) was carried out to see if this "soft" electron transfer method would yield the 19-electron parent $(OC)_5Fe^{\cdot -}$. However, only the product of dissociative electron transfer, $(OC)_4Fe^{\cdot -}$, was observed (Eq. 14).

$$EtO_2CCHN_2^{\cdot -} + Fe(CO)_5 \;(m/z\ 114) \rightarrow (OC)_4Fe^{\cdot -} + CO + EtO_2CCHN_2 \;(m/z\ 168) \quad (16)$$

An intriguing result was obtained from the reaction of $EtO_2CCHN_2^{\cdot -}$ with the diazo compound c-$C_5H_4{=}N_2$ (reaction 27, Table 1). Although the rate of this reaction was not measured, it appeared to be fast with the exclusive production of the anion radical m/z 92, c-$C_5H_4N_2^{\cdot -}$ (Eq. 17). With thermal electrons, c-$C_5H_4{=}N_2$ undergoes dissociative electron attachment yielding exclusively the carbene anion radical c-$C_5H_4^{\cdot -}$;[1] therefore, EA(c-$C_5H_4{=}N_2$) > D(c-$C_5H_4^-$—$N_2{\cdot}$). However, in the present case, the energy deposited in $C_5H_4N_2^{\cdot -}$ in the electron transfer in Eq. (17) is (EA(c-$C_5H_4{=}N_2$) − EA(EtO_2CCHN_2)) −(excess vibrational energy residual in EtO_2CCHN_2) which is less than D(c-$C_5H_4^-$—$N_2{\cdot}$). This is important in that we will be able to directly compare the thermochemical properties and reactions of a carbene anion radical (c-$C_5H_4^{\cdot -}$)[1] with those of its precursor diazo anion radical (c-$C_5H_4N_2^{\cdot -}$) for the first time.

$$EtO_2CCHN_2^{\cdot -} + \text{c-}C_5H_4{=}N_2 \rightarrow \text{c-}C_5H_4N_2^{\cdot -} + EtO_2CCHN_2 \quad (17)$$

No reaction was observed between $EtO_2CCHN_2^{\cdot -}$ and PhN_3, hexafluorobenzene (C_6F_6), or SF_6.

DISCUSSION

Thermochemical properties of $EtO_2CCHN_2^{\cdot -}$

Using the bracketing method with the series of potential proton donors listed in Table 2 PA ($EtO_2CCHN_2^{\cdot -}$) = 355 ± 4 kcal mol^{-1} was determined. The transition between H_2S and c-C_5H_6 gave this value. The interesting and unusual β-elimination of H_2^+ from CH_3SH by $EtO_2CCHN_2^{\cdot -}$ producing $H_2CS^{\cdot -}$ was presented in the Results.

The fast electron transfer reactions between $EtO_2CCHN_2^{\cdot -}$ with NO_2, ICF_3, $(CF_3)_2C{=}O$, and SO_2 (Table 1) yielding the parent anion radicals of these neutral molecules are summarized in Table 3. These results establish EA(EtO_2CCHN_2) < 25 kcal mol^{-1} (= EA(SO_2)).

The slow reaction ($k_{total} = 2.4 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1}) of $EtO_2CCHN_2^{\cdot -}$ with biacetyl (reaction 19, Table 1) where electron transfer was 23% of k_{total} ($k_{ET} = 5.5 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1}) was indicative of a somewhat endothermic charge transfer process. This suspicion was determined to be correct when we found that electron transfer between $CH_3C({=}O)C({=}O)CH_3^{\cdot -}$ and EtO_2CCHN_2 (Eq. 18) was fast ($k_f = 8.3 \times 10^{-10}$ cm^3 molecule^{-1} s^{-1}). Since we have the forward and reverse rate constants for the equilibrium electron transfer in Eq. (18), we

$$CH_3C({=}O)C({=}O)CH_3^{\cdot -} + EtO_2CCHN_2 \underset{k_r}{\overset{k_f}{\rightleftharpoons}} EtO_2CCHN_2^{\cdot -} + CH_3C({=}O)C({=}O)CH_3 \quad (18)$$

calculate $K = k_f/k_r = 151$ and $\Delta G° = -2.97$ kcal mol^{-1}. Assuming $\Delta S°$ is very small in this equilibrium, $-\Delta G° \sim -\Delta H° =$ EA(EtO_2CCHN_2) − EA (biacetyl).[22] This relationship yields EA(EtO_2CCHN_2) = 19.7 kcal mol^{-1}.

Table 3. Summary of electron transfer (ET) reactions between $EtO_2CCHN_2^{\cdot-}$ and neutral substrates

Neutral substrate	EA (kcal mol^{-1}) of neutral	Expected product(s) of ET	Is ET product(s) observed?
NO_2	53.3[a]	NO_2^-	yes
ICF_3	36.2 ± 4.6[b]	I^-, $ICF_3^{\cdot-}$	yes
$(CF_3)_2C{=}O$	~35[c]	$(CF_3)_2CO^{\cdot-}$	yes
SO_2	25.3 ± 0.8[d]	$SO_2^{\cdot-}$	yes
$CH_3C({=}O)C({=}O)CH_3$	16.7[e]	$CH_3C({=}O)C({=}O)CH_3^{\cdot-}$	yes
SF_6	23 ± 4[e]	$SF_6^{\cdot-}$	no
C_6F_6	$>41.5 \pm 6.9$[f] <41[g]	$C_6F_6^{\cdot-}$	no

[a] Ref. 22.
[b] Ref. 17.
[c] See footnote ‡ on p. 6259.
[d] R. J. Celotta, R. A. Bennett and J. L. Hall, *J. Chem. Phys.* **60**, 1740 (1974).
[e] Ref. 24.
[f] Ref. 27.
[g] See footnote ‡ on p. 6261.

Electron transfer from $EtO_2CCHN_2^{\cdot-}$ to SF_6 (EA = 23 ± 4 kcal mol^{-1})[24] was not observed. While SF_6 readily attaches thermal electrons,[25] the absence of electron transfer to SF_6 in this case is probably associated with the considerable geometry change expected for the anion $SF_6^{\cdot-}$ compared to that of the neutral SF_6 with intersection of the two potential curves.†[24,26] This explanation has been suggested for the fact that perfluoromethylcyclohexane (C_7F_{14}) "does not accept electrons from A^- even when the electron affinity of A is much lower than that of C_7F_{14}".[22] Possibly this factor also explains the absence of electron transfer from $EtO_2CCHN_2^{\cdot-}$ to hexafluorobenzene‡ observed here, but such a geometric change in $C_6F_6^{\cdot-}$ compared to C_6F_6 is difficult to imagine.

Mechanism of the reactions of $EtO_2CCHN_2^{\cdot-}$ *with neutral substrates*

Two different mechanisms were considered for the reactions of $EtO_2CCHN_2^{\cdot-}$ with H^+-donor molecules and carbonyl containing substrates. The first mechanism would involve the intact structure diazo anion radical structure shown in Eq. (19) for H^+-transfer with a HA molecule via formation of the excited collision complex **4**; here we assume protonation occurs on C_α of the diazo anion radical. Since the formation of ion-neutral collision complexes such as **4** is attractive with well depths of 10–20 kcal mol^{-1}, if this energy exceeds $D(EtO_2CCH^-{-}N_2\cdot)$ N_2 would be lost leading to a complex of the carbene anion radical and HA (Eq. 20). In this latter possibility, H^+-transfer from

$$EtO_2CCHN_2^{\cdot-} + HA \rightarrow \underset{\mathbf{4}}{[(EtO_2CCHN_2 \cdot\cdot H \cdot\cdot A)^{\cdot-}]^*} \rightarrow A^- + EtO_2CCH_2N_2\cdot \quad (19)$$

$$\mathbf{4} \rightarrow [(EtO_2CCH \cdot\cdot H \cdot\cdot A)^{\cdot-}]^* + N_2 \quad (20)$$

HA would depend on PA($EtO_2CCH^{\cdot-}$) which could differ significantly from PA($EtO_2CCHN_2^{\cdot-}$). However, observation of the hydrogen bonded clusters $EtO_2CCHN_2^{\cdot-}$/HA where HA = CH_3NO_2, $HOCH_2CF_3$, and $HCCl_3$ demonstrates that the process in Eq. (20) is not important in the H^+-transfer reactions and should not play a role in the reactions of the diazo anion radical with carbonyl containing molecules. Therefore, the results described herein involve the thermochemistry and chemical reactions of $EtO_2CCHN_2^{\cdot-}$.

The majority of the results described for the reactions of $EtO_2CCHN_2^{\cdot-}$ with ketones and esters forming stabilized enolate anions derived from β-keto esters are conveniently summarized as involving addition/fragmentation mechanisms. We consider that the C_α of $EtO_2CC_\alpha HH_2^{\cdot-}$ adds nucleophilically to the carbonyl center of the neutral yielding an excited adduct **5** (Eq. 21). Loss of N_2 from **5** could be stepwise or concerted with radical β-fragmentation of R_1 or R_2 yielding the observed conjugate bases of the β-keto esters. Since these are the same products that would be formed by reaction of the carbene anion radical $EtO_2CCH^{\cdot-}$ with these carbonyl containing neutrals, such product formation *cannot* be utilized in the condensed phase to distinguish between $R_2CN_2^{\cdot-}$ and $R_2C^{\cdot-}$.§ This point should be further clarified by a separate study of $c\text{-}C_5H_4N_2^{\cdot-}$ and comparison of the results with those reported for $c\text{-}C_5H_4^{\cdot-}$.[1]

$$\begin{array}{ll} [EtO_2CCH(N_2\cdot)C(O^-)R_1R_2] \rightarrow & EtO_2CCH{=}C(O^-)R_1 + \cdot R_2 + N_2 \\ \quad \mathbf{5}\downarrow & \\ EtO_2CCH{=}C(O^-)R_2 + \cdot R_1 + N_2 & \end{array} \quad (21)$$

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† We have observed that electron transfer between $CH_3C({=}O)C({=}O)CH_3^{\cdot-}$ and SF_6 can be observed, but it requires addition of large concentrations ($>10^{13}$ molecules/cm^3) of SF_6 to yield $SF_6^{\cdot-}$.

‡ Lifshitz *et al.*[27] assigned EA(C_6F_6) $> 41.5 \pm 6.9$ kcal mol^{-1}. Based on the absence of electron transfer from $c\text{-}C_5H_5^-$ (EA($c\text{-}C_5H_5\cdot$) = 41.2 ± 0.5 kcal mol^{-1})[28] to C_6F_6, EA(C_6F_6) < 41 kcal mol^{-1} was suggested.[12]

§ See Ref. 7 for a discussion of the controversy surrounding intermediacy of $R_2C^{\cdot-}$ vs $R_2CN_2^{\cdot-}$ by electroreduction of diazo compounds in the condensed phase.

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