

# Gas-Phase Ion-Molecule Reactions of Dioxygen Anion Radical ( $O_2^{\cdot-}$ )

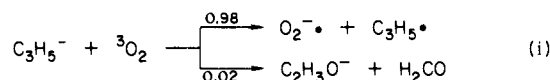
Richard N. McDonald\* and A. Kasem Chowdhury

Contribution from the Department of Chemistry, Kansas State University, Manhattan, Kansas 66506. Received July 26, 1984

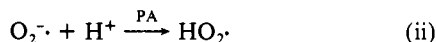
**Abstract:** The gas-phase ion-molecule reactions of dioxygen anion radical ( $O_2^{\cdot-}$ ) with a variety of neutral organic substrates have been studied in a flowing afterglow apparatus. The  $S_N2$  reactions  $O_2^{\cdot-}$  with  $CH_3Br$  and  $CH_3Cl$  yielded  $Br^-$  and  $Cl^-$ , respectively, with rate constants near the collision limit. The reactions of  $O_2^{\cdot-}$  with a series of methyl esters proceed by a major  $S_N2$  displacement channel with the reaction efficiencies ( $k/k_{ADO}$ ) in the order  $CF_3CO_2CH_3 \gg HCO_2CH_3 > H_2C=CHCO_2CH_3 > CH_3CO_2CH_3$ . These facts lead to the conclusion that  $O_2^{\cdot-}$  is intrinsically and kinetically an excellent nucleophile in gas-phase  $S_N2$  displacement reactions with  $CH_3X$  molecules. Termolecular nucleophilic carbonyl addition yielding adduct anion-radicals is observed as minor reaction channels with the esters  $HCO_2CH_3$  and  $CH_3CO_2CH_3$ , and with  $CF_3C(=O)CH_3$ , but is the major channel with the ketones  $(CH_3)_2C=O$  and  $CH_3C(=O)C(=O)CH_3$ . The reaction of  $O_2^{\cdot-}$  with  $(CF_3)_2C=O$  is considered to occur by exclusive electron transfer, giving  $(CF_3)_2CO^{\cdot-}$ . Reaction of  $O_2^{\cdot-}$  with  $H_2C=CHCN$  proceeded stepwise, forming monomeric and dimeric species,  $O_2(CH_2CHCN)_{1,2}^{\cdot-}$ .  $HS^-$  was the only product formed in the reaction of  $O_2^{\cdot-}$  with thiacyclopropane.

As pointed out in a recent review on the chemistry of dioxygen anion radical,  $O_2^{\cdot-}$ , commonly referred to as superoxide anion, "Little was known in 1969 about the reactivity of superoxide in any environment".<sup>1a</sup> This situation has changed dramatically in the intervening years for both the condensed-<sup>1</sup> and gas-phase chemistry<sup>2</sup> of  $O_2^{\cdot-}$ . However, a disparity exists in many of the reaction and reagent types used in the condensed- and gas-phase experiments.

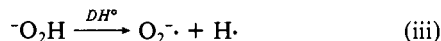
Our interest in determining the *intrinsic* gas-phase organic chemistry of  $O_2^{\cdot-}$  stemmed from our "rediscovery" of a convenient method to generate  $O_2^{\cdot-}$  by electron transfer from allyl anion ( $C_3H_5^-$ ) to  $O_2$  (eq i); this reaction was previously described by



Bohme and Young ( $k = 2.8 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ ).<sup>3</sup> From the thermochemical properties of  $O_2$ ,  $O_2^{\cdot-}$ , and several related molecules ( $EA(O_2) = 10.1 \pm 0.2 \text{ kcal mol}^{-1}$ <sup>4</sup> =  $-\Delta H_f^\circ(O_2^{\cdot-})$ ,  $\Delta H_f^\circ(HO_2) = 2.5 \pm 0.6 \text{ kcal mol}^{-1}$ ,<sup>5</sup>  $\Delta H_f^\circ(HO_2^-) = -24.9 \pm 0.7 \text{ kcal mol}^{-1}$ <sup>6</sup>), values for the proton<sup>7</sup> and H-atom affinities of  $O_2^{\cdot-}$  were calculated (eq ii and iii).



$$PA(O_2^{\cdot-}) = 354.6 \pm 0.8 \text{ kcal mol}^{-1}$$



$$DH^\circ(O_2^{\cdot-}-H) = 66.2 \pm 0.9 \text{ kcal mol}^{-1}$$

$O_2^{\cdot-}$  in aprotic solvents is reported to be a powerful nucleophile in  $S_N2$  displacement reactions with primary and secondary alkyl

halides yielding ultimately dialkyl peroxides along with the product of elimination.<sup>1a</sup> As we will show, high nucleophilicity carries over to the gas phase in the reactions of  $O_2^{\cdot-}$  with  $CH_3X$  derivatives. This feature of the gas-phase chemistry of  $O_2^{\cdot-}$  coupled with its low PA (this is similar to PA's of  ${}^{\cdot}CN$ ,  $HS^-$ , and  $c-C_3H_5^-$ ,<sup>8</sup> which are kinetically modest<sup>9</sup> to weak<sup>10</sup>  $S_N2$  nucleophiles) makes  $O_2^{\cdot-}$  *unique* among gas-phase  $S_N2$  nucleophiles studied to date. That is  $O_2^{\cdot-}$  functions similar to  $HO^-$ ,  $CH_3O^-$ , and  $O^-$  in  $S_N2$  reactivity with  $CH_3X$  derivatives<sup>9,11</sup> while it is a relatively weak base and, as an open-shell nucleophile, has a low H-atom affinity. The fact that most of these nucleophilic displacement reactions at  $sp^3$  carbon are only modestly exothermic<sup>9,11</sup> also points to  $O_2^{\cdot-}$  being a "super"  $S_N2$  nucleophile.

## Experimental Section

The reported gas-phase studies were carried out in a flowing afterglow (FA) apparatus with a modular flow tube similar to that previously described.<sup>12</sup> The FA and the modified ion production region are shown in Figure 1.  $NH_3$  was added via inlet 1 and undergoes dissociative electron attachment producing  $H_2N^{\cdot-}$  ( $m/z$  16) contaminated with  $HO^-$  ( $m/z$  17). Efforts to predry the  $NH_3$  did not eliminate  $m/z$  17. The concentration of  $NH_3$  was restricted so that formation of ammonia cluster ions ( $m/z$  34 ( $HO^-/NH_3$ ) and 33 ( $H_2N^{\cdot-}/NH_3$ )) represented less than 2% of the signal intensity for  $m/z$  16. Propene was added via inlet 2 and underwent fast  $H^+$  transfer with  $H_2N^{\cdot-}$  and  $HO^-$  ( $k = 2.5 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ )<sup>13</sup> producing allyl anion,  $C_3H_5^-$  ( $m/z$  41).  $O_2$  was introduced via inlet 4 which is 25 cm downstream from the mixing juncture of  $H_2N^{\cdot-}/HO^-$  with  $C_3H_6$ . Fast electron transfer between  $C_3H_5^-$  and  $O_2$  produced  $O_2^{\cdot-}$  ( $m/z$  32) and a trace of  $C_2H_3O^-$  ( $m/z$  43).<sup>3</sup> The flow continued uninterrupted for 30 cm where collisional stabilization of vibrationally excited  $O_2^{\cdot-}$  ions with the buffer gas occurs prior to reaching the neutral inlet port and the desired ion-molecule reaction commences. The ion-molecule reaction distance (neutral inlet to first sampling nose cone<sup>12</sup>) was 62.5 cm.

Following addition of  $O_2$  to the flow of  $C_3H_5^-$ , small signals for a number of background anions,  $m/z$  26 (1%), 35 and 37 ( $Cl^-$ , 3%), 41 (0.5%), 43 (2%), 46 (2%), 48 and 49 (1%), and 50 (1%), were observed in the mass range of 4 to 200 amu. The signal intensities for these background anions are unchanged in the faster reactions of  $O_2^{\cdot-}$  reported ( $k \geq 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ ) while the signal intensities of the ions  $m/z$

(1) (a) Sawyer, D. T.; Valentine, J. S. *Acc. Chem. Res.* **1981**, *14*, 393-400 and references therein. (b) Further comments and reference can be found in correspondence by Fridovich (Fridovich, I. *Acc. Chem. Res.* **1982**, *15*, 200) and rebuttal by Sawyer (Sawyer, D. T.; Valentine, J. S. *Ibid.* **1982**, *15*, xxx).

(2) See Albritton (Albritton, D. L. *At. Data Nucl. Data Tables* **1978**, *22*, 1-101) for a summary of ion-molecule reactions measured in flow reactors through 1977.

(3) Bohme, D. K.; Young, L. B. *J. Am. Chem. Soc.* **1970**, *92*, 3301-3309.

(4) (a) Celotta, R. J.; Bennett, R. A.; Hall, J. L.; Siegel, M. W.; Levine, J. *Phys. Rev.* **1972**, *A6*, 631-642. The  $EA(O_2)$  agrees with several values listed by: (b) Drzaic, P. S.; Jeffrey, M.; Brauman, J. I. In "Gas Phase Ion Chemistry"; Bowers, M. T., Ed.; Academic Press: New York, 1979; Vol. 3, Chapter 21. (c) Phelps, A. V.; Pack, J. L. *Phys. Rev. Lett.* **1961**, *6*, 111-113. (d) Rosenstock, H. M.; Draxl, K.; Steiner, B. W.; Herron, J. T. *J. Phys. Chem. Ref. Data, Suppl. 1* **1977**, *6*. Rosenstock et al. give  $\Delta H_f^\circ(O_2^{\cdot-}) = -10.1 \text{ kcal mol}^{-1}$ . (e) Stull, D. R.; Prophet, H. "JANAF Thermochemical Tables", *Natl. Stand. Ref. Data Ser., Natl. Bur. Stand.* **1971**, No. 37— $\Delta H_f^\circ_{298}(O_2^{\cdot-}) = -11.39 \pm 0.5 \text{ kcal mol}^{-1}$ .

(5) Howard, C. J. *J. Am. Chem. Soc.* **1980**, *102*, 6937-6941.

(6) Bierbaum, V. M.; Schmitt, R. J.; DePuy, C. H.; Mead, R. D.; Schulz, P. A.; Lineberger, W. C. *J. Am. Chem. Soc.* **1981**, *103*, 6262-6263.

(7)  $\Delta H_f^\circ(H^+) = 367.2 \text{ kcal mol}^{-1}$ .<sup>4e</sup>

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

(9) Tanaka, K.; Mackay, G. I.; Payzant, J. D.; Bohme, D. K. *Can. J. Chem.* **1976**, *54*, 1643-1659.

(10) McDonald, R. N.; Chowdhury, A. K.; Setser, D. W. *J. Am. Chem. Soc.* **1981**, *103*, 7586-7589.

(11) Olmstead, W. N.; Brauman, J. I. *J. Am. Chem. Soc.* **1977**, *99*, 4219-4228.

(12) (a) McDonald, R. N.; Chowdhury, A. K. *J. Am. Chem. Soc.* **1983**, *105*, 2194-2203. (b) McDonald, R. N.; Chowdhury, A. K.; Setser, D. W. *Ibid.* **1980**, *102*, 6491-6498.

(13) (a) Bierbaum, V. M.; DePuy, C. H.; Shapiro, R. H.; Stewart, J. H. *J. Am. Chem. Soc.* **1976**, *98*, 4229-4235. (b) Mackay, G. I.; Lien, M. H.; Hopkinson, A. C.; Bohme, D. K. *Can. J. Chem.* **1978**, *56*, 131-140.

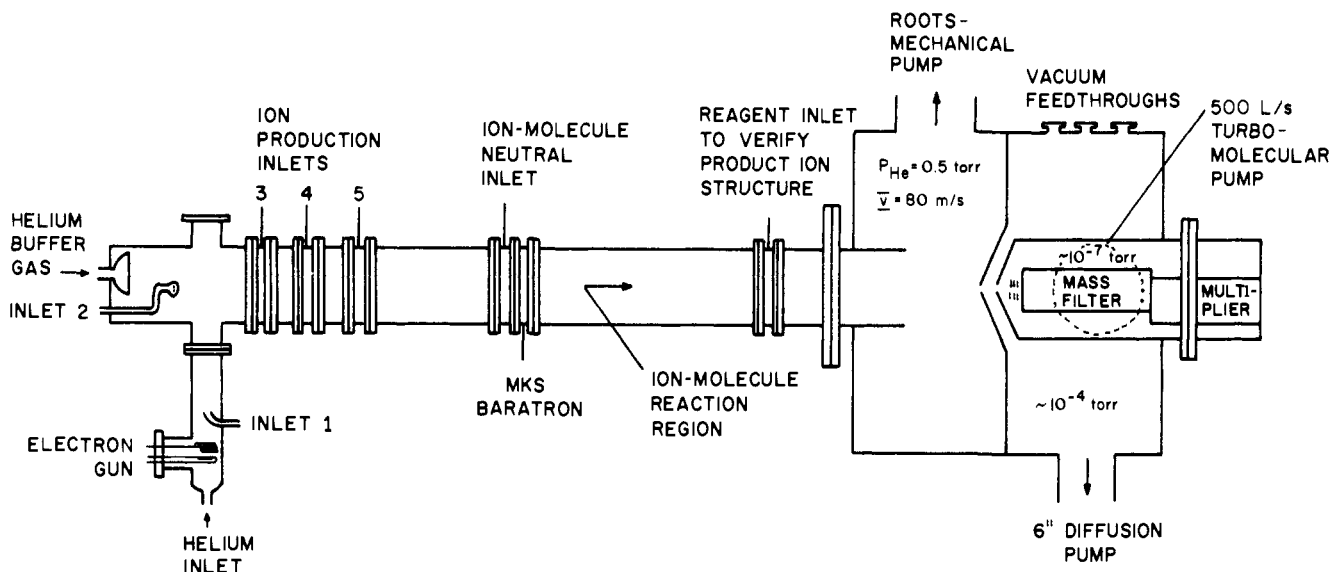


Figure 1. Flowing afterglow apparatus with a modular flow tube and the modified ion production region.

41, 43, 46, 48, 49, and 50 are reduced slightly in the slower reactions with  $O_2^-$ . Thus, the observed product ions are those exclusively or principally ( $\geq 97\%$ ) formed in the  $O_2^-$ -neutral molecule reaction.

Helium was the buffer gas in these experiments with 75% inducted into the upstream end of the flow tube and 25% added below the electron gun (Figure 1). The buffer gas pressure ( $P_{He}$ ) and flow velocity ( $\bar{v}$ ) were maintained by a large, fast-pumping system. These two parameters could be varied from  $P_{He} = 0.3$ –1.2 torr and  $\bar{v} = 36$ –80  $m\ s^{-1}$  by adjusting the outlet gate valve and/or altering the helium inlet flow. At  $P_{He} = 1.0$  torr, the composition of the flow at the neutral inlet port was  $[He] = 3.2 \times 10^{16}$  atoms  $cm^{-3}$ ,  $[NH_3] = [C_3H_6] \approx 10^{12}$  molecules  $cm^{-3}$ , and  $[O_2] = 10^{13}$  molecules  $cm^{-3}$  with  $[O_2^-] \sim 10^8$  ions  $cm^{-3}$ . Determination of the bimolecular rate constants for ion-molecule reactions is straightforward under pseudo-first-order conditions (excess neutral molecule concentration) with a fixed reaction distance (time) by methods and equations previously given.<sup>12b</sup>

The helium used in this study was 99.99% pure, supplied by Welders Products, and was further purified by passage through two traps filled with Davis 4A molecular sieves cooled with liquid nitrogen and then warmed to room temperature in a glass coil prior to introduction into the flow tube. All of the gas and liquid neutral substrates used were obtained from commercial sources. The liquid substrates were freshly distilled, and a constant boiling center-cut was transferred to a gas storage bulb following 3 freeze-pump-thaw degassing cycles. The gas substrates were used directly.

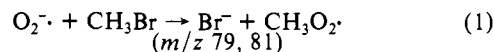
## Results

**Generation of  $O_2^-$ .** The reaction selected for generation of  $O_2^-$  was that of allyl anion ( $C_3H_5^-$ ) with  $O_2$  (eq 1). In our hands, this reaction gave  $O_2^-$  ( $m/z$  32) along with a trace of  $C_2H_3O^-$  ( $m/z$  43), considered to be the enolate anion  $H_2C=CHO^-$ ,<sup>3</sup> and was very fast,  $k = 3.0 \times 10^{-10}$   $cm^3\ molecule^{-1}\ s^{-1}$  ( $P_{He} = 0.5$  torr,  $\bar{v} = 80$   $m\ s^{-1}$ ), being 43% of the collision limit<sup>14</sup> ( $k_{ADO} = 7.0 \times 10^{-10}$   $cm^3\ molecule^{-1}\ s^{-1}$ ). Bohme and Young<sup>3</sup> were unable to reconcile their results of this fast reaction with known EA's of  $O_2$  and  $C_3H_5$ . The recent experimentally determined  $EA(C_3H_5) = 8.3 \pm 0.5$  kcal  $mol^{-1}$  by Professor Barney Ellison<sup>15</sup> taken with  $EA(O_2) = 10.1 \pm 0.2$  kcal  $mol^{-1}$ <sup>4</sup> allows for a slightly exothermic electron transfer between the two reactants.

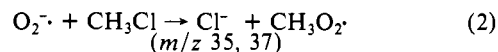
The kinetic, product, and  $\Delta H^\circ$  data for the ion-molecule reactions of  $O_2^-$  with neutral organic substrates are summarized in Table I. In all cases, clean pseudo-first-order decay plots of log ion signal of  $O_2^-$  ( $m/z$  32) vs. concentration of neutral

reactants were observed. No  $P_{He}$  dependence was observed for these reactions when the flow parameters were changed from  $P_{He} = 0.5$  torr and  $\bar{v} = 80$   $m\ s^{-1}$  to  $P_{He} = 1.0$  torr and  $\bar{v} = 40$   $m\ s^{-1}$  unless otherwise noted. For reactions involving exclusive or partial termolecular reaction channels, the apparent bimolecular rate constants are given. The rate constants for the collision-limited ion-molecule reactions were calculated by using the average dipole orientation theory,  $k_{ADO}$ .<sup>14</sup>

**Reactions of  $O_2^-$  with Alkyl Halides.** To determine the gas-phase kinetic nucleophilicity of  $O_2^-$  in  $S_N2$  displacement reactions,<sup>9,11</sup> the reactions of  $O_2^-$  with  $CH_3X$  molecules were examined (reactions 1–3, Table I). The reaction of  $O_2^-$  with  $CH_3Br$  yielding  $Br^-$  (eq 1) proceeded at nearly the collision limit ( $k_{ADO}$ ). The



exothermicity of this product-forming channel is  $\Delta H^\circ(1) = -24.9$  kcal  $mol^{-1}$ .<sup>16–18</sup> The reaction of  $O_2^-$  with  $CH_3Cl$  producing  $Cl^-$  (eq 2) was also fast being 35% of the calculated collision limit. The exothermicity of eq 2 was  $\Delta H^\circ(2) = -17.0$  kcal  $mol^{-1}$ .<sup>16–18</sup>



The related  $S_N2$  displacement of  $O_2^-$  with  $CH_3F$  yielding  $F^-$  cannot occur under our experimental conditions since this channel is strongly endothermic,  $\Delta H^\circ = +13.3$  kcal  $mol^{-1}$ .<sup>17,18</sup> However, a very slow reaction at the lower limit of detection in the FA was observed when  $CH_3F$  was added to the flow containing  $O_2^-$  at  $P_{He} = 1.0$  torr and  $\bar{v} = 40$   $m\ s^{-1}$ ,  $k \sim 3 \times 10^{-13}$   $cm^3\ molecule^{-1}\ s^{-1}$ . The product ion was the sum of the masses of the reactants  $m/z$  66 and is considered to be the collisionally stabilized ion-dipole collision complex  $O_2^-/CH_3F$  which structurally may closely approximate the transition state for the  $S_N2$  displacement reaction. However, we hasten to point out that a number of other structures may better represent this anion-radical complex. That even a trace of the collision complex survives the conditions of the experiment, passage through orifices in two sampling nose cones, ion lenses, and the quadrupole rods with varying potentials on each component, is remarkable. The data require that three out of every 10 000 collisions remain in the attractive ion-dipole potential well

(14) Su, T.; Bowers, M. T. *J. Chem. Phys.* **1973**, *58*, 3027–3037; *Int. J. Mass Spectrom. Ion Phys.* **1973**, *12*, 347–356.

(15) Personal communication from Professor Barney Ellison from the PES of  $C_3H_5^-$ : Oakes, J. M.; Ellison, G. B. *J. Am. Chem. Soc.* **1984**, *106*, 7734–7741. This new value of  $EA(C_3H_5)$  is about 0.2 eV lower than that reported by Zimmerman (Zimmerman, A. H.; Brauman, J. I. *J. Am. Chem. Soc.* **1977**, *99*, 3656–3568) using photodetachment of  $C_3H_5^-$  in the trapped ion cell of an ICR spectrometer ( $EA(C_3H_5) = 0.550 \pm 0.054$  eV).

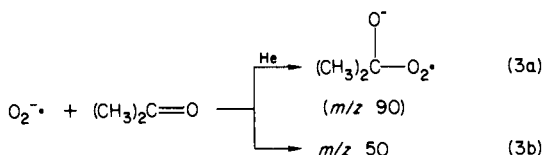
(16) Cox, J. D.; Pilcher, G. "Thermochemistry of Organic and Organometallic Compounds"; Academic Press: New York, 1970.  $\Delta H_f^\circ(CH_3Br) = -9.1 \pm 0.3$  kcal  $mol^{-1}$ ;  $\Delta H_f^\circ(CH_3Cl) = -20.5 \pm 0.1$  kcal  $mol^{-1}$ .

(17)  $\Delta H_f^\circ(X^-)$  calculated from  $\Delta H_f^\circ(X)$ <sup>18</sup> and  $EA(X)$ ;  $\Delta H_f^\circ(Br^-) = -50.8$  kcal  $mol^{-1}$ ;  $\Delta H_f^\circ(Cl^-) = -54.4$  kcal  $mol^{-1}$ ;  $\Delta H_f^\circ(F^-) = -59.5$  kcal  $mol^{-1}$ .

(18) Benson, S. W. "Thermochemical Kinetics", 2nd ed.; Wiley-Interscience: New York, 1976;  $\Delta H_f^\circ(CH_3O_2) = +6.7$  kcal  $mol^{-1}$ ;  $\Delta H_f^\circ(C_2H_5O_2) = -1.8$  kcal  $mol^{-1}$ ;  $\Delta H_f^\circ(CH_3F) = -36 \pm 2$  kcal  $mol^{-1}$ .

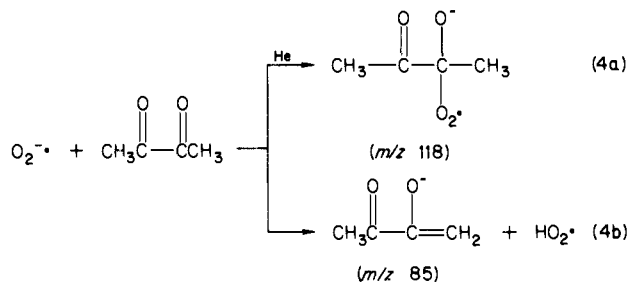
(considered to be 10–20 kcal mol<sup>-1</sup> deep) on the ion-molecule potential surface. The lifetime of the collision complex must be  $>10^{-7}$  s to enable several collisions between it and the buffer gas and other neutrals present in the flow to cool the complex below the energy of the inlet channel.

**Reactions of  $O_2^-$  with Ketones.** The reaction of  $O_2^-$  with acetone (reaction 3) is, in part, understandable and, in part, somewhat of a mystery. The major ion product is  $m/z$  90 which is the sum of the masses of  $O_2$  and acetone. We believe this species is the bound tetrahedral adduct of nucleophilic carbonyl addition shown in eq 3.<sup>19</sup> This structural assignment is supported by the increase in  $m/z$  90 at  $P_{He} = 1.0$  torr (87%) compared to the



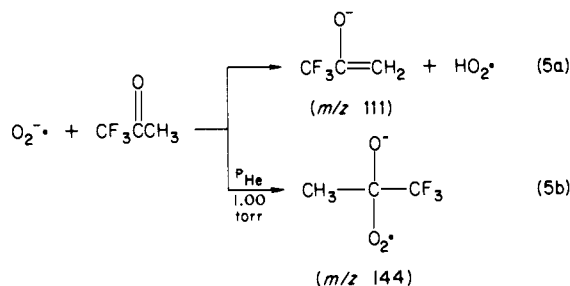
amount formed at  $P_{He} = 0.5$  torr (79%) with no change in the rate constant. The ion product  $m/z$  50 appears to be the monohydrate cluster ion  $O_2^- \cdot H_2O$  which is slowly formed in the separate ion-molecule reaction of  $O_2^-$  with  $H_2O$ . Addition of  $D_2O$  to  $m/z$  50 yields the exchanged cluster  $m/z$  52 ( $O_2^- \cdot D_2O$ ). Despite repeated and varied attempts to "dry" the acetone prior to and during distillation, formation of  $m/z$  50 remained as a product ion.

While the termolecular addition of  $O_2^-$  to acetone occurred with only a modest rate constant, the reaction of  $O_2^-$  with biacetyl (reaction 4) was fast and produced the adduct  $m/z$  118 (major) and the enolate anion  $m/z$  85 (minor). At  $P_{He} = 1.0$  torr, a small signal ( $\sim 2\%$ ) at  $m/z$  86 was observed which may be the ketyl



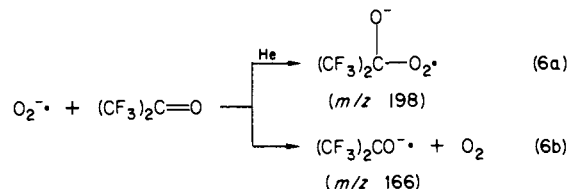
anion radical of biacetyl,  $C_4H_6O^-$ , the product of electron transfer. We have separately shown that biacetyl readily attaches electrons in the FA, yielding  $m/z$  86. Formation of the enolate anion  $m/z$  85 requires that  $\Delta H_{acid}^\circ(CH_3C(=O)C(O^-)CH_3) < 355$  kcal mol<sup>-1</sup>, the latter value being  $PA(O_2^-) = \Delta H_{acid}^\circ(HO_2)$ . Observation of  $m/z$  86 means that  $EA(CH_3C(=O)C(=O)CH_3) \sim EA(O_2)$ . Nucleophilic addition to a carbonyl group of biacetyl was expected to be much faster than with acetone since we had demonstrated this kinetic point in the reactions of these ketones with phenylnitrene anion radical ( $PhN^-$ ).<sup>20</sup> However, the present examples require termolecular collisional stabilization of the adduct product rather than the radical  $\beta$ -fragmentation pathway available to the adduct formed from the reaction with  $PhN^-$ .<sup>20</sup>

The reaction of  $O_2^-$  with  $CF_3C(=O)CH_3$  at  $P_{He} = 0.5$  torr proceeded at the collision limit ( $k_{ADO} = k_{total}$ ) exclusively by  $H^+$  transfer, producing the enolate anion  $CF_3C(O^-)=CH_2$ ,  $m/z$  111. By increasing  $P_{He}$  to 1.0 torr, 10% of the adduct  $m/z$  144 was observed (eq 5). We believe that these results demonstrate that nucleophilic addition to carbonyl groups can occur competitive with other reaction channels, e.g., exothermic  $H^+$  transfer (eq 5a,  $\Delta H^\circ = -4.3 \pm 2$  kcal mol<sup>-1</sup>).<sup>8</sup> However, adduct formation will only be observed if collisional stabilization of the adduct can occur



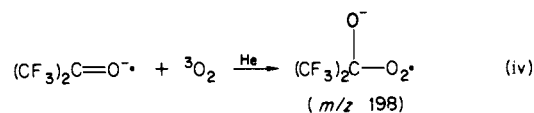
efficiently which depends on the structure and lifetime of the adduct, and on the nature of the bath gas components.

The reaction of  $O_2^-$  with  $(CF_3)_2C=O$  also occurred at the collision limit,  $k_{ADO}$ , yielding approximately equal amounts of the adduct anion radical ( $m/z$  198) and  $(CF_3)_2CO^-$  ( $m/z$  166), the product of electron transfer (eq 6). The electron affinity (EA)



of  $(CF_3)_2C=O$  is estimated to be  $\sim 33$  kcal mol<sup>-1</sup> since electron transfer was observed as a minor channel in the reaction of this ketone with  $PhN^-$ .<sup>20</sup> ( $EA(PhN) = 33.7 \pm 0.3$  kcal mol<sup>-1</sup> kcal mol<sup>-1</sup>).<sup>21</sup> Using  $EA((CF_3)_2CO) = 33$  kcal mol<sup>-1</sup>,  $\Delta H^\circ$  (reaction 6b) =  $-23$  kcal mol<sup>-1</sup> if  ${}^3O_2({}^3\Sigma_g^-)$  is formed, but it is thermally neutral if  ${}^1O_2({}^1\Delta_g)$  is the product.<sup>22</sup> Formation of the adduct  $m/z$  198 is also believed to be exothermic,  $\Delta H^\circ$ (reaction 6a)  $\sim -35$  kcal mol<sup>-1</sup>.<sup>23</sup>

In an attempt to better understand the processes in reaction 6, we have prepared  $(CF_3)_2CO^-$  ( $m/z$  166) by electron attachment with  $(CF_3)_2C=O$  at the electron gun in the FA. Addition of  ${}^3O_2$  to the flow containing only  $m/z$  166 produced the adduct  $m/z$  198 (eq iv), but with a small rate constant,  $k = 1.2 \times 10^{-11}$  cm<sup>3</sup> molecule<sup>-1</sup> at  $P_{He} = 0.5$  torr,  $\bar{v} = 80$  m s<sup>-1</sup>, and 1.0 torr,  $\bar{v} = 32$  m s<sup>-1</sup> ( $k_{ADO} = 5.7 \times 10^{-10}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>).<sup>14</sup> The absence of  $P_{He}$  dependence on this reaction indicates that saturation of



this termolecular reaction has occurred at our lowest pressure. Although reaction iv has a low efficiency ( $k/k_{ADO} = 0.02$ ), we have  $10^{13}$  molecules cm<sup>-3</sup> of  ${}^3O_2$  present in the flow from the preparation of  $O_2^-$  when reaction 6 is carried out. This suggests that a major source of the adduct  $m/z$  198 is the secondary reaction of  $(CF_3)_2CO^-$  with  ${}^3O_2$ . Therefore, we believe that the principal (or exclusive) primary reaction between  $O_2^-$  and  $(CF_3)_2C=O$  is electron transfer (reaction 6b). The electronic state of the neutral dioxygen produced in this electron transfer reaction 6b is unknown.

**Reactions of  $O_2^-$  with Esters.** The reactions of  $O_2^-$  with simple alkyl esters have two primary reaction channels available,  $S_N2$  displacement (or E2 elimination with ethyl esters) at the etheral alkyl group and nucleophilic addition at the carbonyl carbon. With

(21) Drzagic, P. S.; Brauman, J. I. *J. Am. Chem. Soc.* **1984**, *106*, 3443–3446.

(22)  $\Delta H_f^\circ({}^1O_2({}^1\Delta_g)) = 22.5$  kcal mol<sup>-1</sup>; Foote, C. S. *Acc. Chem. Res.* **1968**, *1*, 104–110.

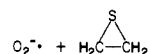
(23)  $\Delta H_f^\circ((CF_3)_2C=O) = -336.2$  kcal mol<sup>-1</sup> (calcd)<sup>18</sup> using the group equivalent value  $C(F_3)(CO) = -152.4$  kcal mol<sup>-1</sup>;  $\Delta H_f^\circ((CF_3)_2(O^-)OO^-) = -381.2$  kcal mol<sup>-1</sup> (calcd)<sup>18</sup> assuming  $\Delta H_{acid}^\circ(ROH) = 347.4$  kcal mol<sup>-1</sup><sup>24</sup> and  $DH^\circ(ROO-H) = 90$  kcal mol<sup>-1</sup>.

(24)  $\Delta H_{acid}^\circ((CF_3)_2CHOH) = 348.4 \pm 2$  kcal mol<sup>-1</sup> has been derived from  $\Delta G_{acid}^\circ((CF_3)_2CHOH) = 340.8 \pm 2$  kcal mol<sup>-1</sup> (Professor R. W. Taft, private communication) assuming  $\Delta S_{acid}^\circ((CF_3)_2CHOH) = \Delta S_{acid}^\circ(CF_3CH_2OH) = 25.5$  cal mol<sup>-1</sup> deg<sup>-1</sup>.<sup>8</sup>

(19) See McDonald (McDonald, R. N.; Chowdhury, A. K. *J. Am. Chem. Soc.* **1983**, *105*, 7267–7271) for characterization of adducts formed by nucleophilic addition of  $F_3C^-$  to various carbonyl-containing molecules of ketones and esters in the gas phase.

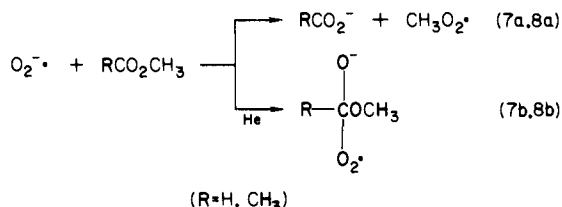
(20) McDonald, R. N.; Chowdhury, A. K. *J. Am. Chem. Soc.* **1983**, *105*, 198–207.

**Table I.** Summary of Kinetic and Product Data for the Ion-Molecule Reactions of the Dioxide Anion Radical with Certain Neutral Organic Molecules

re-action no.	ion + neutral reactants	→	products [assumed neutral]	fraction of product ion signal	$\Delta H^\circ,^a$ kcal mol <sup>-1</sup>	$k_{\text{total}},^b$ cm <sup>3</sup> molecule <sup>-1</sup> s <sup>-1</sup>	$k_{\text{ADO}},^c$ cm <sup>3</sup> molecule <sup>-1</sup> s <sup>-1</sup>
1	O <sub>2</sub> <sup>-•</sup> + CH <sub>3</sub> Br	→	Br <sup>-</sup> [+ CH <sub>3</sub> O <sub>2</sub> <sup>-</sup> ]	1.00	-24.9	1.3 × 10 <sup>-9</sup>	1.7 × 10 <sup>-9</sup>
2	O <sub>2</sub> <sup>-•</sup> + CH <sub>3</sub> Cl	→	Cl <sup>-</sup> [+ CH <sub>3</sub> O <sub>2</sub> <sup>-</sup> ]	1.00	-17.0	7.4 × 10 <sup>-10</sup>	1.9 × 10 <sup>-9</sup>
3a	O <sub>2</sub> <sup>-•</sup> + (CH <sub>3</sub> ) <sub>2</sub> C=O	$\xrightarrow{\text{He}}$	(CH <sub>3</sub> ) <sub>2</sub> C(O)O <sub>2</sub> <sup>-•</sup>	0.79 (0.87) <sup>f</sup>		2.3 × 10 <sup>-11</sup>	2.6 × 10 <sup>-9</sup>
3b		→	<i>m/z</i> 50 (O <sub>2</sub> <sup>-•</sup> /H <sub>2</sub> O)	0.21 (0.13) <sup>f</sup>			
4a	O <sub>2</sub> <sup>-•</sup> + CH <sub>3</sub> C(=O)C(=O)CH <sub>3</sub>	$\xrightarrow{\text{He}}$	CH <sub>3</sub> C(=O)C(CH <sub>3</sub> )(O)O <sub>2</sub> <sup>-•</sup>	0.90		1.4 × 10 <sup>-9</sup>	1.4 × 10 <sup>-9</sup>
4b		→	H <sub>2</sub> C=C(O <sup>-</sup> )C(=O)CH <sub>3</sub> [+ HO <sub>2</sub> <sup>-</sup> ]	0.10			
5a	O <sub>2</sub> <sup>-•</sup> + CF <sub>3</sub> C(=O)CH <sub>3</sub>	→	H <sub>2</sub> C=C(O <sup>-</sup> )CF <sub>3</sub> [+ HO <sub>2</sub> <sup>-</sup> ]	1.00 (0.90) <sup>f</sup>	-4.3	2.2 × 10 <sup>-9</sup>	1.5 × 10 <sup>-9</sup>
5b		$\xrightarrow{\text{He}}$	(CF <sub>3</sub> )(CH <sub>3</sub> )C(O)O <sub>2</sub> <sup>-•</sup> at <i>P</i> <sub>He</sub> = 1.0 torr	(0.10) <sup>f</sup>			
6	O <sub>2</sub> <sup>-•</sup> + (CF <sub>3</sub> ) <sub>2</sub> C=O	$\xrightarrow{\text{He}}$	(CF <sub>3</sub> ) <sub>2</sub> C(O)O <sub>2</sub> <sup>-•</sup> + (CF <sub>3</sub> ) <sub>2</sub> CO <sup>-•</sup> [+ O <sub>2</sub> ]	see text	~-35 <sup>d</sup>	2.0 × 10 <sup>-9</sup>	1.7 × 10 <sup>-9</sup>
7a	O <sub>2</sub> <sup>-•</sup> + HCO <sub>2</sub> CH <sub>3</sub>	→	HCO <sub>2</sub> <sup>-</sup> [+ CH <sub>3</sub> O <sub>2</sub> <sup>-</sup> ]	0.90	-12.1	1.0 × 10 <sup>-10</sup>	1.9 × 10 <sup>-9</sup>
7b		$\xrightarrow{\text{He}}$	H(CH <sub>3</sub> O)C(O)O <sub>2</sub> <sup>-•</sup>	0.10			
8a	O <sub>2</sub> <sup>-•</sup> + CH <sub>3</sub> CO <sub>2</sub> CH <sub>3</sub>	→	CH <sub>3</sub> CO <sub>2</sub> <sup>-</sup> [+ CH <sub>3</sub> O <sub>2</sub> <sup>-</sup> ]	0.91 (0.72) <sup>f</sup>	-7.7	3.8 × 10 <sup>-12</sup>	1.9 × 10 <sup>-9</sup>
8b		$\xrightarrow{\text{He}}$	CH <sub>3</sub> (CH <sub>3</sub> O)C(O)O <sub>2</sub> <sup>-•</sup>	0.09 (0.28) <sup>f</sup>			
9a	O <sub>2</sub> <sup>-•</sup> + CF <sub>3</sub> CO <sub>2</sub> CH <sub>3</sub>	→	CF <sub>3</sub> CO <sub>2</sub> <sup>-</sup> [+ CH <sub>3</sub> O <sub>2</sub> <sup>-</sup> ]	0.98	-32.5	2.3 × 10 <sup>-9</sup>	2.4 × 10 <sup>-9</sup>
9b		→	CF <sub>3</sub> C(=O)O <sub>2</sub> <sup>-•</sup> [+ CH <sub>3</sub> O <sup>-</sup> ]	0.02			
10a	O <sub>2</sub> <sup>-•</sup> + CF <sub>3</sub> CO <sub>2</sub> C <sub>2</sub> H <sub>5</sub>	→	CF <sub>3</sub> CO <sub>2</sub> <sup>-</sup> [+ C <sub>2</sub> H <sub>5</sub> O <sub>2</sub> <sup>-</sup> ]	0.98	-32.5 <sup>e</sup>	2.6 × 10 <sup>-9</sup>	2.4 × 10 <sup>-9</sup>
10b		→	CF <sub>3</sub> C(=O)O <sub>2</sub> <sup>-•</sup> [+ C <sub>2</sub> H <sub>5</sub> O <sup>-</sup> ]	0.02			
11	O <sub>2</sub> <sup>-•</sup> + H <sub>2</sub> C=CHCO <sub>2</sub> CH <sub>3</sub>	→	H <sub>2</sub> C=CHCO <sub>2</sub> <sup>-</sup> [+ CH <sub>3</sub> O <sub>2</sub> <sup>-</sup> ]	1.00		1.7 × 10 <sup>-11</sup>	2.0 × 10 <sup>-9</sup>
12	O <sub>2</sub> <sup>-•</sup> + H <sub>2</sub> C=CHCN	$\xrightarrow{\text{He}}$	O <sub>2</sub> (CH <sub>2</sub> CHCN) <sub>1,2</sub> <sup>-•</sup>	1.00		1.0 × 10 <sup>-10</sup>	3.3 × 10 <sup>-9</sup>
13	O <sub>2</sub> <sup>-•</sup> + 	→	HS <sup>-</sup> [+ H <sub>2</sub> C=CHO <sub>2</sub> <sup>-</sup> ]	1.00		6.5 × 10 <sup>-10</sup>	

<sup>a</sup>Data for  $\Delta H^\circ$ 's are found in the introduction and in ref 7, 8, 16-18, and 29. <sup>b</sup> $k_{\text{total}}$ 's were determined at *P*<sub>He</sub> = 0.5 torr and  $\bar{v}$  = 80 m s<sup>-1</sup>, and checked at *P*<sub>He</sub> = 1.0 torr and  $\bar{v}$  = 40 m s<sup>-1</sup>. No *P*<sub>He</sub> dependence was observed except where noted.  $k_{\text{total}}$ 's are estimated to be accurate to ±30%. <sup>c</sup>Reference 14. <sup>d</sup>Reference 23. <sup>e</sup>Assumed to be that of reaction 9a. <sup>f</sup>Product data obtained at *P*<sub>He</sub> = 1.0 torr and  $\bar{v}$  = 40 m s<sup>-1</sup>.

HCO<sub>2</sub>CH<sub>3</sub> (reaction 7), the fast reaction with O<sub>2</sub><sup>-•</sup> occurred by both of these pathways, forming HCO<sub>2</sub><sup>-</sup> (*m/z* 45), assumed by S<sub>N</sub>2 displacement at CH<sub>3</sub> (major), and carbonyl addition, yielding the adduct *m/z* 92 (minor). No *P*<sub>He</sub> dependency was observed



on either the product branching fraction or the rate constant within experimental error.

Formation of HCO<sub>2</sub><sup>-</sup> (*m/z* 45) as the major product in a reasonably fast, exothermic reaction channel was expected on the basis of the results of the reactions with CH<sub>3</sub>Br and CH<sub>3</sub>Cl, and other CH<sub>3</sub>X molecules to be presented. It was, therefore, surprising to learn that Johlman and Wilkins<sup>25</sup> observed no anionic products in their reaction of O<sub>2</sub><sup>-•</sup> with HCO<sub>2</sub>CH<sub>3</sub> at low pressure (10<sup>-7</sup> torr) in the trapped ion cell of their Fourier transform mass spectrometer. Since the presence of ~10% HCO<sub>2</sub>H in our sample of HCO<sub>2</sub>CH<sub>3</sub> could produce our results, we have established the absence of HCO<sub>2</sub>H with the following results. (a) The <sup>1</sup>H NMR spectrum of the distilled, center-cut sample of HCO<sub>2</sub>CH<sub>3</sub> showed that HCO<sub>2</sub>H was absent prior to loading the ester sample into its storage bulb on the gas-handling rack for the FA. (b) Reaction of this sample of HCO<sub>2</sub>CH<sub>3</sub> (used to obtain data in reaction 7, Table I) with Ph<sub>2</sub>C<sup>-•</sup> (PA = 382 kcal mol<sup>-1</sup>), a poor S<sub>N</sub>2 nucleophile, produced exclusively Ph<sub>2</sub>C=C(O<sup>-</sup>)H, *m/z* 195, by nucleophilic carbonyl addition followed by radical β-fragmentation with loss of <sup>•</sup>OCH<sub>3</sub>,<sup>26</sup> H<sup>+</sup> transfer between HCO<sub>2</sub>H ( $\Delta H^\circ_{\text{acid}}$  = 345 kcal mol<sup>-1</sup>) and Ph<sub>2</sub>C<sup>-•</sup> occurring at the collision limit is exothermic by 37 kcal mol<sup>-1</sup>. (c) Addition of excess HCO<sub>2</sub>CH<sub>3</sub>

to the flow containing HCO<sub>2</sub><sup>-</sup> (*m/z* 45) and the adduct H(CH<sub>3</sub>O)C(O)O<sub>2</sub><sup>-•</sup> (*m/z* 92) from the reaction of O<sub>2</sub><sup>-•</sup> with HCO<sub>2</sub>CH<sub>3</sub> does not yield the cluster ion in HCO<sub>2</sub><sup>-</sup>/HCO<sub>2</sub>H (*m/z* 91) which is rapidly formed when HCO<sub>2</sub>H is added to a flow containing HCO<sub>2</sub><sup>-</sup>. Only a slight decay of several of the background ions (see Experimental Section) was observed which together would account for ≤4% of the observed HCO<sub>2</sub><sup>-</sup> signal intensity. Therefore, we conclude that the primary processes in the reaction of O<sub>2</sub><sup>-•</sup> with HCO<sub>2</sub>CH<sub>3</sub> are bimolecular S<sub>N</sub>2 displacement yielding HCO<sub>2</sub><sup>-</sup> and competitive termolecular addition producing the adduct H(CH<sub>3</sub>O)C(O)O<sub>2</sub><sup>-•</sup> (eq 7).

We are unable to reconcile these results of a reasonably fast S<sub>N</sub>2 reaction channel in the FA at *P*<sub>He</sub> = 0.5 and 1.0 torr with the total absence of this channel at 10<sup>-7</sup> torr in the FTMS experiment,<sup>25</sup> assuming that O<sub>2</sub><sup>-•</sup> produced in both systems is in the same electronic and vibrational state. We are confident that ground-state O<sub>2</sub><sup>-•</sup> (<sup>2</sup>Π<sub>g</sub>) is formed in the present FA experiments since electron transfer between C<sub>3</sub>H<sub>5</sub><sup>-</sup> and O<sub>2</sub> is only ~2 kcal mol<sup>-1</sup> exothermic. The multiple collisions of O<sub>2</sub><sup>-•</sup> (<sup>2</sup>Π<sub>g</sub>) with the bath gas (He/NH<sub>3</sub>/C<sub>3</sub>H<sub>6</sub>/O<sub>2</sub>) should remove any excess vibrational energy in the O<sub>2</sub><sup>-•</sup> (<sup>2</sup>Π<sub>g</sub>) as demonstrated by the absence of *P*<sub>He</sub> dependence on this and other rate constants and branching ratios of bimolecular channels.

Calculations of the excited states of O<sub>2</sub><sup>-•</sup> indicate that the <sup>4</sup>Σ<sub>u</sub><sup>-</sup> and <sup>2</sup>Π<sub>u</sub> excited states are energetically feasible in the FTMS study especially with electron attachment to O<sub>2</sub> with 6 eV electrons.<sup>25</sup> Kebarle et al.<sup>28</sup> have shown that S<sub>N</sub>2 reactions with  $k_{\text{obsd}} < k_{\text{coll}}$  have a negative temperature dependence. However, we do not know if electronic or vibrationally excited states of O<sub>2</sub><sup>-•</sup> contribute to the absence of this S<sub>N</sub>2 reaction in the FTMS.

The slower reaction of O<sub>2</sub><sup>-•</sup> with CH<sub>3</sub>CO<sub>2</sub>CH<sub>3</sub> (reaction 8) followed similar reaction channels, but in this case the branching fraction was *P*<sub>He</sub> dependent. At *P*<sub>He</sub> = 0.5 torr,  $\bar{v}$  = 80 m s<sup>-1</sup>, the ratio of CH<sub>3</sub>CO<sub>2</sub><sup>-</sup> (*m/z* 59)/CH<sub>3</sub>(CH<sub>3</sub>O)C(O)O<sub>2</sub><sup>-•</sup> (*m/z* 106) was 91/9, while at *P*<sub>He</sub> = 1.0 torr,  $\bar{v}$  = 41 m s<sup>-1</sup> this ratio was 72/28. These latter data establish the competitive termolecular addition and bimolecular displacement channels in the reaction of O<sub>2</sub><sup>-•</sup> with CH<sub>3</sub>CO<sub>2</sub>CH<sub>3</sub>.

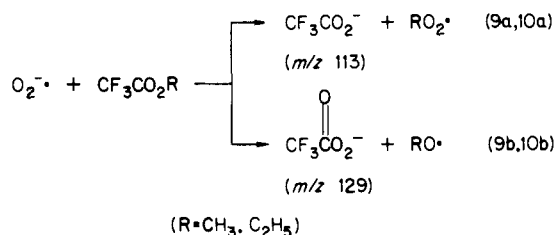
(25) Johlman, C. L.; Wilkins, C. L. *J. Am. Chem. Soc.* **1985**, *107*, 327-332. We thank Professor Wilkins for a preprint and discussions of the FTMS results.

(26) Ph<sub>2</sub>C<sup>-•</sup> is prepared in the FA from Ph<sub>2</sub>C=N<sub>2</sub> by dissociative electron attachment: W. Y. Gung, MS Thesis, Kansas State University, 1984. The details of the PA,  $\Delta H_f^\circ$ , and chemical reaction of Ph<sub>2</sub>C<sup>-•</sup> will be the subject of another publication.

(27) Krauss, M.; Neumann, D.; Wahl, A. C.; Das, G.; Zemke, W. *Phys. Rev. A* **1973**, *7*, 69-77.

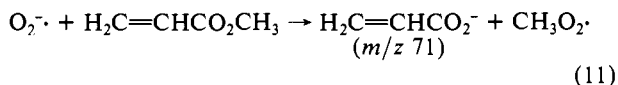
(28) Caldwell, G.; Magnera, T. F.; Kebarle, P. *J. Am. Chem. Soc.* **1984**, *106*, 959-966.

The reactions of  $O_2^-$  with methyl and ethyl trifluoroacetate were similar to each other, but they added a new wrinkle to the carbonyl addition chemistry. As expected, the major primary channel appears to be  $S_N2$  displacement on the alkyl group of the



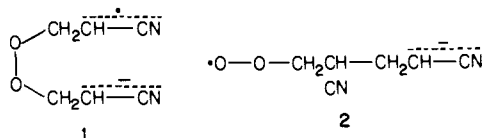
ester yielding  $CF_3CO_2^-$  ( $m/z$  113). We believe this is also the mechanism of the major reaction channel with the ethyl ester (reaction 10a) even though E2 elimination giving  $CF_3CO_2^- + C_2H_4 + HO_2^\bullet$  is modestly exothermic ( $\Delta H^\circ = -13.3$  kcal mol $^{-1}$ ). The minor primary product ion  $m/z$  129 from both of these reactions is most reasonably represented as the conjugate base of peroxytrifluoroacetic acid,  $CF_3C(=O)OO^-$ . Its formation can be rationalized by anionic fragmentation of the carbonyl adduct  $[CF_3C(O^-)(O_2)OR]$ , giving the complex  $[CF_3C(=O)O_2^-/OR]$  which undergoes electron transfer yielding the complex  $[CF_3C(=O)O_2^-/OR]$  followed by separation to give the observed product ion. This mechanism requires  $EA(CF_3C(=O)O_2^-) > EA(RO^\bullet)^{29}$  which appears reasonable. That this type of adduct fragmentation is unique with the  $CF_3CO_2R$  reactions and not observed with  $HCO_2CH_3$  or  $CH_3CO_2CH_3$  may simply reflect differences in  $EA(CF_3C(=O)O_2^-) > EA(HC(=O)O_2^-)$  and  $EA(CH_3C(=O)O_2^-)$ ; the strongly basic  $CH_3O^-$  will not be ejected from the latter two adducts.

The reaction of  $O_2^-$  with methyl acrylate proceeded with a modest rate constant exclusively by  $S_N2$  displacement, yielding the carboxylate anion  $m/z$  71 (reaction 11). This result will be discussed later in the context of  $S_N2$  reactions of  $O_2^-$  with  $CH_3X$  molecules.



**Reactions of  $O_2^-$  with Acrylonitrile and Thiacyclopropane.** Since  $O_2^-$  failed to oligomerize methyl acrylate, the reaction of  $O_2^-$  with the more reactive vinyl monomer acrylonitrile was examined. We observed a fast decay of the  $O_2^-$  signal and initial formation of a monomeric species  $m/z$  85 ( $O_2CH_2CHCN^-$ ). As further  $H_2C=CHCN$  was added the signal for  $m/z$  85 decreased and the signal for a dimeric species  $m/z$  138 rapidly increased. No further oligomerization was observed. A trace of  $m/z$  26 ( $CN^-$ ) was also formed in this process.

The apparent termination of this oligomerization at a dimeric species is in marked contrast to the oligomerization of  $H_2C=C-HCN$  initiated by  $^-CH_2CN$  which terminated at the tetramer,  $NCCH_2(-CH_2CH(CN))_3-CH_2CHCN^-$ .<sup>30</sup> Such early termination indicates that the dimeric anion radical  $m/z$  138 has undergone molecular rearrangement, generating a more stable anion radical which is not effective in further propagation steps.<sup>12a,30</sup> This rules out structures **1** and **2** as the observed forms of  $m/z$

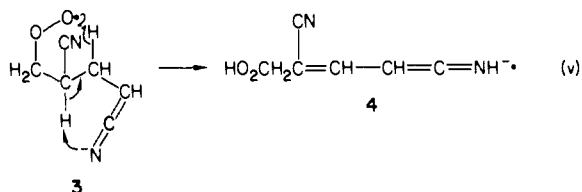


138. We favor structure **2** as the initially formed dimeric  $m/z$  138 due to the similarity in the fast first initiation rate constants

(29) Engelking (Engelking, P. C.; Ellison, G. B.; Lineberger, W. C. *J. Chem. Phys.* **1978**, *69*, 1826-1832) report  $EA(CH_3O^\bullet) = 36.2 \pm 0.5$  kcal mol $^{-1}$ .

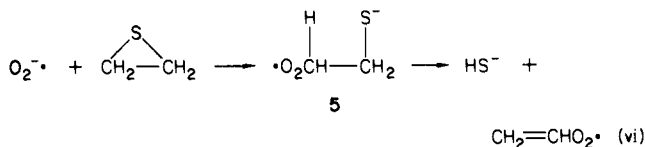
(30) McDonald, R. N.; Chowdhury, A. K. *J. Am. Chem. Soc.* **1982**, *104*, 2675-2676.

with  $O_2^-$  and  $^-CH_2CN$  as initiators and the equally fast propagation step.<sup>30</sup> Using a pseudobicyclic conformer of **2**, **3**, for convenience, we speculate that the stable  $m/z$  138 is the  $\pi$ -an-



ion/radical **4** shown in eq v. The two steps of  $H^+$  and H-atom transfer would probably proceed separately rather than concerted. The delocalized cyano-substituted, unsaturated ketenimine structure of neutral **4** could well have a positive EA (EA(maleic anhydride) =  $9.2 \pm 4.6$  kcal mol $^{-1}$ )<sup>4b</sup> and be expected to be unreactive in propagation reactions with  $H_2C=CHCN$ .

The fast reaction of  $O_2^-$  with thiacyclopropane produced  $HS^-$  ( $m/z$  33) exclusively;  $^{34}S$  was observed as  $m/z$  35 ( $M+2$ ) which was 4.3% of the  $m/z$  33 signal intensity (theory 4.4%). We believe  $HS^-$  is formed by initial nucleophilic, exothermic ring opening of thiacyclopropane with  $O_2^-$  giving **5** followed by elimination of  $HS^-$  producing the vinyl peroxy radical as a byproduct (eq vi).<sup>31</sup>



## Discussion

**Nucleophilicity of  $O_2^-$  in  $S_N2$  Displacement Reactions.** The experimental and theory of  $S_N2$  reactions in the gas phase have been summarized by several authors,<sup>20,28,32</sup> and recently the temperature dependence on these anionic displacement reactions was measured for several alkyl bromides reacting with  $Cl^-$ .<sup>28</sup> Bohme et al.<sup>9</sup> developed a simple kinetic scale of  $S_N2$  nucleophilicity for anionic nucleophiles based on their apparent activation energies (derived from  $k_{\text{expt}} = k_{\text{ADO}} \exp(-E_a/RT)$ ) and their variation with exothermicity of the reaction with  $CH_3X$  ( $X = F, Cl, Br$ ). Using this approach, we calculate  $E_a = 0.16$  kcal mol $^{-1}$  ( $\Delta H^\circ = -24.9 \pm 0.5$  kcal mol $^{-1}$ )<sup>16-18</sup> for the  $O_2^- + CH_3Br$  reaction and  $E_a = 0.56$  kcal mol $^{-1}$  ( $\Delta H^\circ = -17.0 \pm 0.3$  kcal mol $^{-1}$ )<sup>16-18</sup> for the reaction of  $O_2^-$  with  $CH_3Cl$ . The  $S_N2$  displacement reaction of  $O_2^- + CH_3F \rightarrow F^- + CH_3O_2^\bullet$  is reasonably endothermic ( $\Delta H^\circ = +13.3 \pm 2.2$  kcal mol $^{-1}$ )<sup>16-18</sup> and thus could not be observed. Although these calculated barriers are undoubtedly too low,<sup>32</sup> based on this analysis of the  $S_N2$  reactions with  $CH_3Br$  and  $CH_3Cl$ , we conclude that  $O_2^-$  is kinetically a strong gas-phase nucleophile and ranks with other strong anionic nucleophiles (i.e.,  $H^-$ ,  $F^-$ ,  $HO^-$ ,  $H_2N^-$ ,  $CH_3O^-$ , and  $CH_3NH^-$ ) in this reaction type and relative comparison.<sup>9,11</sup>

This is in spite of the fact that these reaction exothermicities are considerably smaller than those with the other powerful nucleophiles studied.<sup>9,11</sup> The low thermodynamic basicity of  $O_2^-$  ( $PA(O_2^-) = 354.6 \pm 0.8$  kcal mol $^{-1}$ ) and low methyl cation affinity ( $O_2^- + CH_3^+ \rightarrow CH_3O_2^\bullet$ ,  $\Delta H^\circ = -245$  kcal mol $^{-1}$ ) contrast these thermochemical properties of other strong anionic oxygen nucleophiles, e.g.,  $CH_3O^-$  ( $PA = 379.2 \pm 2$  kcal mol $^{-1}$ ) and  $CH_3^+$ -affinity = 270 kcal mol $^{-1}$ ).<sup>8</sup> These factors are paralleled in the smaller  $\Delta H^\circ$ 's for the reactions of  $O_2^-$  with  $CH_3X$  molecules. Thus, the high  $S_N2$  nucleophilicity of  $O_2^-$  is anomalous using the usual parameters to define this "property". Pellerite and Brauman<sup>32</sup> have used Marcus theory combined with RRKM calculations to model intrinsic nucleophilicities of anions with  $CH_3X$  molecules in  $S_N2$  reactions. They suggested that the fast reaction of  $CH_3O^-$  with  $CH_3Cl$  has a high intrinsic barrier which

(31) McDonald, R. N.; Chowdhury, A. K. *Macromolecules* **1982**, *15*, 1640-1641.

(32) Pellerite, M. J.; Brauman, J. I. *J. Am. Chem. Soc.* **1983**, *105*, 2672-2680, and previous papers by Prof. Brauman's group.

**Table II.** Reactivity of  $O_2^-$  with  $CH_3X$  Molecules in  $S_N2$  Displacement Reactions Yielding  $X^-$  and Assumed Neutral  $CH_3O_2^-$ .

$CH_3X$	% $S_N2$ channel	$\Delta H^\circ$ , kcal/mol	reaction efficiency <sup>a</sup>	$\Delta H^\circ_{acid}(HA) = PA(A^-)$ , <sup>b</sup> kcal/mol
$CF_3CO_2CH_3$	97	-32.5	0.92	323
$CH_3Br$	100	-24.9	0.76	324
$CH_3Cl$	100	-17.0	0.39	333
$HCO_2CH_3$	90	-12.1	0.05	345
$H_2C=CHCO_2CH_3$	100		0.03	
$CH_3CO_2CH_3$	90	-7.1	0.002	349

<sup>a</sup> The fraction of  $k_{total}$  due to  $S_N2$  displacement divided by  $k_{ADO}$ .  
<sup>b</sup> Reference 8.

is compensated for by a large  $CH_3^+$ -affinity of  $CH_3O^-$  (large exothermicity), giving the observed low kinetic reaction barrier. Since the  $S_N2$  displacement reaction of  $O_2^-$  with  $CH_3Cl$  proceeds with a small thermodynamic contribution to lowering the intrinsic barrier, *the intrinsic barrier for this reaction must also be small.* From these arguments, we conclude that  $O_2^-$  is intrinsically a powerful ("super") nucleophile in  $S_N2$  processes.<sup>1a</sup>

In Table I, the results with four methyl esters are also of interest in this discussion. These esters are  $HCO_2CH_3$  (reaction 7),  $CH_3CO_2CH_3$  (reaction 8),  $CF_3CO_2CH_3$  (reaction 9), and  $H_2C=CHCO_2CH_3$  (reaction 11). The reactions of  $O_2^-$  with the first three of these methyl esters occurred mainly by  $S_N2$  displacement, yielding the carboxylate anion with a minor channel involving carbonyl addition. The order of reactivity of  $O_2^-$  with those esters by this mechanism is listed in Table II. Here we see a correlation between the reaction efficiency of these three processes with the  $\Delta H^\circ$  for the reaction<sup>33</sup> and  $\Delta H^\circ_{acid}(RCO_2H)$ <sup>8</sup>, reflecting the leaving group abilities of the  $RCO_2^-$  products.<sup>11</sup>

The results obtained with  $H_2C=CHCO_2CH_3$  strongly suggest that  $\Delta H^\circ_{acid}(H_2C=CHCO_2H) = 347 \pm 2$  kcal mol<sup>-1</sup>, intermediate between  $\Delta H^\circ_{acid}(CH_3CO_2H)$  and  $\Delta H^\circ_{acid}(HCO_2H)$ .<sup>8</sup> This modest change in  $\Delta H^\circ_{acid}$  between  $CH_3CO_2H$  and  $H_2C=CHCO_2H$  compared to  $C_6H_5CO_2H$  ( $\Delta H^\circ_{acid} = 338.8 \pm 2$  kcal mol<sup>-1</sup>)<sup>8</sup> is quite different from the condensed-phase  $pK_a$ 's ( $H_2O$ , 25°C) of these three acids ( $CH_3CO_2H$ ,  $pK_a = 4.76$ ;  $H_2C=CHCO_2H$ ,  $pK_a = 4.25$ ; and  $C_6H_5CO_2H$ ,  $pK_a = 4.20$ ).<sup>34</sup> If this estimate of  $\Delta H^\circ_{acid}(H_2C=CHCO_2H)$  is correct, the similarity of the vinyl and phenyl substituents on the acidity of the carboxylic acid group in the condensed phase is due to solvation effects.

**Nucleophilicity of  $O_2^-$  in Carbonyl Addition Reactions.** Direct comparison of the nucleophilicity of  $O_2^-$  in bimolecular  $S_N2$  displacement reactions with methyl esters and termolecular carbonyl addition is not justified due to the limited data and  $P_{He}$  variations used in this study. The single obvious point is that these two different nucleophilic processes remain competitive (at least partially) even in the reactions occurring at the collision limit (reactions 9 and 10, Table I).

(33) Additional thermochemical values (in kcal mol<sup>-1</sup>) used in the  $\Delta H^\circ_{acid}(HCO_2CH_3) = -83.6$ ,<sup>18</sup>  $\Delta H^\circ_{acid}(CH_3CO_2CH_3) = -98.0$ ,<sup>18</sup> and  $\Delta H^\circ_{acid}(CF_3CO_2CH_3) = -240.7$ .<sup>20</sup>

(34) Brown, H. C.; McDaniel, D. H.; Hafliger, O. In "Determination of Organic Structures by Physical Methods"; Braude, E. A., Nachold, F. C., Eds.; Academic Press: New York, 1955; Chapter 14.

In the reactions of  $O_2^-$  with the four ketones investigated, adduct formation appears to be the exclusive product channel with acetone (ignoring formation of  $m/z$  50, reaction 3) and was competitive with  $H^+$  transfer with  $t$ -acetyl (reaction 4) and to a lesser extent with  $CF_3C(=O)CH_3$  (reaction 5), but apparently not with electron transfer to  $(CF_3)_2C=O$  (reaction 6; see Results section). If we assume similar termolecular collisional stabilization efficiencies with the buffer gas components and the tetrahedral adducts formed by  $O_2^-$  adding to the ketones, we find that nucleophilic carbonyl addition follows the order  $CF_3COCH_3 > CH_3COCOCH_3 > CH_3COCH_3$ . This simplifying assumption ignores factors such as variations in steric effects and changes in the number and the energy levels of the density of states of the different vibrationally excited adducts produced. However, this order is approximately that followed in the  $k_{rel}^{C=O}$ 's for the reaction of  $PhN^-$  with these ketones:  $CH_3COCOCH_3 > CF_3COCH_3 \gg CH_3COCH_3$ .<sup>20</sup> In these latter reactions, nucleophilic carbonyl addition is rapidly followed by radical  $\beta$ -fragmentation of acetyl or methyl radicals, respectively, from the tetrahedral anion-radical adduct. With the esters, methyl formate and acetate, it appears that addition of  $O_2^-$  to  $HCO_2CH_3$  is faster than with  $CH_3CO_2CH_3$  which is the same order of  $k_{rel}^{C=O}$  observed in the reactions of these esters with  $PhN^-$ .<sup>20</sup> Unfortunately, the termolecular addition reactions of  $F_3C^-$  with  $CH_3CO_2CH_3$  and  $HCO_2CH_3$  cannot be used as a direct comparison in the present termolecular reactions since the Riveros reaction<sup>25,35</sup> with the stronger base  $F_3C^-$  and  $HCO_2CH_3$  swamped that reaction (96% of the product channels).<sup>19</sup>

**Summary.** We have found that  $O_2^-$  is *both kinetically and intrinsically* a powerful nucleophile in gas-phase  $S_N2$  displacement reactions. Since  $O_2^-$  is a weak base in the gas phase, we have been able to examine  $S_N2$  reactions with a larger range of  $CH_3X$  molecules than previously possible with all other anions of high kinetic nucleophilicity. The resulting correlations of reaction efficiency vs.  $X^-$  leaving group and reaction exothermicity are similar to those observed in the condensed phase.

$O_2^-$  adds to the carbonyl group of ketones and esters forming adducts. This may occur directly by nucleophilic addition or stepwise, involving initial electron transfer if the electron affinity of the carbonyl-containing molecule is greater than that of dioxygen.

The present results offer additional insight into the gas-phase chemistry of  $O_2^-$  previously reported.<sup>36,37</sup>

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**Registry No.**  $C_2H_5^-$ , 1724-46-5;  $O_2$ , 7782-44-7;  $O_2^-$ , 12185-07-8;  $CH_3Br$ , 74-83-9;  $CH_3Cl$ , 74-87-3;  $(CH_3)_2C=O$ , 67-64-1;  $CH_3C(=O)C(=O)CH_3$ , 431-03-8;  $CF_3C(=O)CH_3$ , 421-50-1;  $(CF_3)_2C=O$ , 684-16-2;  $HCO_2CH_3$ , 107-31-3;  $CH_3CO_2CH_3$ , 79-20-9;  $CF_3CO_2CH_3$ , 431-47-0;  $CF_3CO_2C_2H_5$ , 383-63-1;  $H_2C=CHCO_2CH_3$ , 96-33-3;  $H_2C=CHCN$ , 107-13-1;  $H_2CSCH_2$ , 420-12-2.

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