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Generation, Thermodynamics, and Chemistry of the Diphenylcarbene Anion Radical ($Ph_2C^{\cdot -}$)

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Abstract: Dissociative electron attachment with $Ph_2C{=}N$ produced $Ph_2C^{\bullet -}$ (*m/z* 166). The reactions of $Ph_2C^{\bullet -}$ with potential proton donors of known gas-phase acidity were used to bracket PA($Ph_2C^{\bullet -}$) = 380 ± 2 kcal mol^{-1} from which $\Delta H_f{}^{\circ}(Ph_2C^{\bullet -})$ = 81.8 ± 2 kcal mol^{-1} was calculated. The reactions of $Ph_2C^{\bullet -}$ with CH_3OH and C_2H_5OH proceeded with major and minor amounts, respectively, of a $H_2{}^{\bullet +}$-transfer channel, forming Ph_2CH_2, RCHO, and an electron. The kinetic nucleophilicity of $Ph_2C^{\bullet -}$ in S_N2 displacement reactions with CH_3X and C_2H_5X molecules was shown to be *medium*, which requires a significant intrinsic barrier in these reactions. The reactions of $Ph_2C^{\bullet -}$ with various aldehydes, ketones, and esters were fast and established two principal product-forming channels: (1) H^+ transfer if the neutral reactant contains activated C–H bonds and (2) carbonyl addition followed by radical β-fragmentation of one of the groups originally attached to the carbonyl carbon. The order for the ease of radical β-fragmentation in the tetrahedral intermediates was RO > alkyl ≫ H, and $CO_2CH_3 > CH_3$. Since the reactions of $Ph_2C^{\bullet -}$ with the simple esters HCO_2CH_3 and $CH_3CO_2CH_3$ were fast, it should now be possible to examine the reactions of carbonyl-containing organic molecules, which are expected to react slower than these esters and obtain their relative reactivities.

Addition reactions of closed-shell nucleophiles to substrate molecules to yield adducts or products derived from those adducts are an important class of reactions in chemistry. Frequently, studies of the kinetics of the addition step are complicated by the reversibility of this step. It occurred to R.N.M. several years ago that if the structure of the nucleophile was such that the resulting adduct formed by nucleophilic addition would undergo a fast follow-up unimolecular chemical reaction other than retro-addition, the kinetics of the addition step could be measured. This idea was one reason for the beginning of our program to generate and study the chemistry of the class of reactive intermediates termed *hypovalent negative ions* (HNI) in which carbene and nitrene anion radicals are subclasses. Since such species could react as nucleophiles, bases, and/or free radicals, it appeared most reasonable to carry out such studies in the gas phase to avoid the swamping out of desired chemistry by reactions with solvent molecules.

Our previous studies of the reactions of the HNI molecule phenylnitrene anion radical ($PhN^{\bullet -}$) with a series of carbonyl-containing organic molecules showed that the major product-forming channel was that of carbonyl addition followed by radical β-fragmentation;[1] the negative ion product of the reaction was the conjugate base of an acyl anilide shown in eq 1. In that study,

$$PhN^{\bullet -} + R_2C{=}O \rightarrow [Ph\dot{N}{-}C(O^-)R_2] \rightarrow PhN{=}C(O^-)R + {}^{\bullet}R \quad (1)$$

the reactivity of carbonyl groups in organic molecules was RCHO > $R_2C{=}O$ > RCO_2R'. However, we were unable to investigate neutral organic molecules, which react slower than $CH_3CO_2CH_3$ since its rate with $PhN^{\bullet -}$ was already at the lower limit of our technique. Since a number of functional groups lie in the reactivity region less than that of the simple esters (e.g. amides and imides), it was of interest to see whether other HNI molecules could be generated that would be useful in investigating this lower region of reactivity.

The rather low proton affinity (basicity) of $PhN^{\bullet -}$ (PA = 372 ± 2 kcal mol^{-1})[2] was considered most important in reducing or eliminating the competing side reaction of H^+ transfer with activated CH bonds in the neutral organic reactant. This led us to consider non-carbon-centered HNIs first. However, the results that were obtained in the research group with $Ph_2C^{\bullet -}$ appeared to reduce the effect of this parameter *if the rate constant for carbonyl addition was competitive with that of H^+ transfer*. This is undoubtedly the result of the relatively slower rates for H^+ transfer between carbon-centered acids and bases as the reaction approaches thermal neutrality.[3]

Experimental Section

The present experiments were carried out in a flowing afterglow (FA) apparatus, which was previously described.[4] $Ph_2C^{\bullet -}$ was prepared by dissociative electron attachment with $Ph_2C{=}N_2$ in the upstream end of the flow tube. The high-boiling diazo compound was added via an inlet located 10 cm downstream of the electron gun. $Ph_2C{=}N_2$ was loaded into a reservoir that was directly attached to this inlet. When an on–off valve separating the inlet and the reservoir was opened, a sufficient concentration of the vapors of the diazo compound entered the FA to attach all of the thermal energy electrons generated by the electron gun and thermalized in the buffer gas within 10 cm of the inlet port. This was tested by the addition of SF_6 to the flow tube, 15 cm downstream of the diazo compound inlet port; the absence of a signal of $SF_6{}^{\bullet -}$ established the absence of electrons beyond this point in the flow. In this manner, a strong ion signal of $Ph_2C^{\bullet -}$ (*m/z* 166) was observed.

The *m/z* 166 ions were thermalized by collisions with the helium buffer gas (P_{He} = 0.5 Torr, $\bar{v}$ = 80 m s^{-1}) in the next 45 cm of the flow tube. An inlet is located at this point through which the neutral reactant molecules are added, and the desired ion–molecule reaction occurs in the final 65 cm of the flow tube. The fast flow is established and maintained by a large, fast pumping system during the duration of the experiment. The flow is sampled through orifices in two nose cones into a differentially pumped compartment containing a quadrupole mass filter and electron multiplier, which continuously monitor the ion composition in the flow. The structures of the neutral products of the ion–molecule reactions are assumed on the basis of thermochemistry and mass balance since they are not directly observed.

Kinetics of the bimolecular ion–molecule reactions of the *m/z* 166 ions with added neutral reactants, N, were determined under pseudo-first-order conditions where the concentration of [N] (>10^{11} molecules cm^{-3}) was in large excess over that of the ion concentration (<10^8 ions cm^{-3}). We maintained the generation of the *m/z* 166 ions and the 65-cm-long reaction distance, which in a flow experiment is directly related to time, as constants and varied the concentration of [N] added to the flow. At each new [N], we measured the intensities of the signals for the *m/z* 166 ion and the product ion(s). From a plot of log (*m/z* 166) signal vs increasing concentration of [N] added to the flow, the resulting linear decay of the *m/z* 166 ions was then transformed into the bimolecular rate constant by equations already given.[4]

The helium used in this study was of 99.99% purity as supplied by Welders Products, Topeka, KS, and was further purified by passage

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[1] McDonald, R. N.; Chowdhury, A. K. *J. Am. Chem. Soc.* **1983**, *105*, 198.

[2] McDonald, R. N.; Chowdhury, A. K.; Setser, D. W. *J. Am. Chem. Soc.* **1981**, *103*, 6599.

[3] Farneth, W. E.; Brauman, J. I. *J. Am. Chem. Soc.* **1976**, *98*, 7891.

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

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Table I. Summary of Kinetic and Product Data for the Ion–Molecule Reactions of the Diphenylcarbene Anion Radical ($Ph_2C^{\bullet -}$)

	neutral reactants	→	product ion + [assumed neutral]	fraction of product ion signal	k_{total},[a] cm^3 $molecule^{-1}$ s^{-1}	reaction efficiency[b]
1	HC_2H	→	$HC_2^- + [Ph_2CH^{\bullet}]$	1.00	3.7×10^{-10}	0.43
2	n-$C_3H_7C_2H$	→	$C_3H_7C_2^- + [Ph_2CH^{\bullet}]$	1.00	1.6×10^{-10}	0.16[d]
3	CH_3C_2H	→	$CH_3C_2^- + [Ph_2CH^{\bullet}]$	1.00	1.9×10^{-11}	0.017
4	$(CH_3)_2CHOH$	→	$(CH_3)_2CHO^- + [Ph_2CH^{\bullet}]$	1.00	6.3×10^{-10}	0.48
5	C_2H_5OH	→	$C_2H_5O^- + [Ph_2CH^{\bullet}]$	1.00[c]	8.5×10^{-10}	0.61
6	CH_3OH	→	$CH_3O^- + [Ph_2CH^{\bullet}]$	1.00[c]	1.0×10^{-9}	0.71
7	$C_6H_5CH(CH_3)_2$	→	$C_6H_5C(CH_3)_2^- + [Ph_2CH^{\bullet}]$	1.00	not measd	
8	$C_6H_5CH_3$	→	$C_6H_5CH_2^- + [Ph_2CH^{\bullet}]$	1.00	not measd	
9	p-$CH_3C_6H_4CH_3$	→	no reaction		$<10^{-13}$	
10	$CH_3CH{=}CH_2$	→	no reaction		$<10^{-13}$	
11	H_2O	→	no reaction		$<10^{-13}$	
12	CH_3Br	→	$Br^- + [Ph_2\dot{C}CH_3]$	1.00	3.9×10^{-10}	0.35
13	CH_3Cl	→	$Cl^- + [Ph_2\dot{C}CH_3]$	1.00	3.2×10^{-11}	0.025
14	C_2H_5Br	→	$Br^- + [Ph_2\dot{C}C_2H_5]$ or $[Ph_2CH^{\bullet} + CH_2{=}CH_2]$	1.00	1.3×10^{-10}	0.11
15	C_2H_5Cl	→	$Cl^- + [Ph_2\dot{C}C_2H_5]$ or $[Ph_2CH^{\bullet} + CH_2{=}CH_2]$	1.00	1.4×10^{-12}	0.0009
16a	CH_3CHO	→	$Ph_2C{=}C(O^-)H + [CH_3^{\bullet}]$	0.50	8.8×10^{-10}	0.49
16b		→	$CH_2{=}C(O^-)H + [Ph_2CH^{\bullet}]$	0.50		
17a	C_2H_5CHO	→	$Ph_2C{=}C(O^-)H + [C_2H_5^{\bullet}]$	0.54	8.2×10^{-10}	0.48
17b		→	$CH_3CH{=}C(O^-)H + [Ph_2CH^{\bullet}]$	0.46		
18	$(CH_3)_3CCHO$	→	$Ph_2C{=}C(O^-)H + [(CH_3)_3C^{\bullet}]$	1.00	6.5×10^{-10}	0.66[d]
19a	CH_3COCH_3	→	$CH_3C(O^-){=}CH_2 + [Ph_2CH^{\bullet}]$	0.90	6.3×10^{-10}	0.35
19b		→	$Ph_2C{=}C(O^-)CH_3 + [CH_3^{\bullet}]$	0.10		
20	CF_3COCH_3	→	$CF_3C(O^-){=}CH_2 + [Ph_2CH^{\bullet}]$	1.00	1.0×10^{-9}	1.00[d]
21a	$CH_3COCOCH_3$	→	$CH_3COC(O^-){=}CH_2 + [Ph_2CH^{\bullet}]$	0.77	9.4×10^{-10}	1.00
21b		→	$Ph_2C{=}C(O^-)CH_3 + [CH_3CO^{\bullet}]$	0.23		
22a	$CH_3CO_2CH_3$	→	$CH_2{=}C(O^-)OCH_3 + [Ph_2CH^{\bullet}]$	0.97	1.3×10^{-10}	0.10
22b		→	$Ph_2C{=}C(O^-)CH_3 + [CH_3O^{\bullet}]$	0.03		
23	HCO_2CH_3	→	$Ph_2C{=}C(O^-)H + [CH_3O^{\bullet}]$	1.00	1.5×10^{-10}	0.11
24a	$CF_3CO_2CH_3$	→	$Ph_2C{=}C(O^-)CF_3 + [CH_3O^{\bullet}]$	0.81	1.0×10^{-9}	0.71
24b		→	$Ph_2C{=}C(O^-)OCH_3 + [CF_3^{\bullet}]$	0.14		
24c		→	$CF_3CO_2^- + [Ph_2\dot{C}CH_3]$	0.05		
25a	$CF_3CO_2C_2H_5$	→	$Ph_2C{=}C(O^-)CF_3 + [C_2H_5O^{\bullet}]$	0.90	7.0×10^{-10}	0.58
25b		→	$Ph_2C{=}C(O^-)OC_2H_5 + [CF_3^{\bullet}]$	0.10		
26a	$CF_3COSC_2H_5$	→	$Ph_2C{=}C(O^-)CF_3 + [C_2H_5S^{\bullet}]$	0.45	8.8×10^{-10}	0.66
26b		→	$CF_3COS^- + [Ph_2\dot{C}C_2H_5]$ or $[Ph_2CH^{\bullet} + CH_2{=}CH_2]$	0.45		
26c		→	$CF_3COSC_2H_4 + [Ph_2CH^{\bullet}]$	0.10		
27a	$CH_3COCO_2CH_3$	→	$CH_3OCOC(O^-){=}CH_2 + [Ph_2CH^{\bullet}]$	0.33	1.0×10^{-9}	1.00[d]
27b		→	$Ph_2C{=}C(O^-)CH_3 + [CH_3OCO^{\bullet}]$	0.54		
27c		→	$Ph_2C{=}C(O^-)COCH_3 + [CH_3O^{\bullet}]$	0.08		
27d		→	$Ph_2C{=}C(O^-)OCH_3 + [CH_3CO^{\bullet}]$	0.05		
28a	CO_2	$\xrightarrow{He}$	$Ph_2CCO_2^{\bullet -}$	0.99	3.9×10^{-10}	0.60
28b		→	$Ph_2CO^{\bullet -} + [CO]$	0.01		
29a	COS	$\xrightarrow{He}$	$Ph_2CCOS^{\bullet -}$	0.85	4.4×10^{-10}	0.47
29b		→	$Ph_2CS^{\bullet -} + [CO]$	0.15		
30a	CS_2	$\xrightarrow{He}$	$Ph_2CCS_2^{\bullet -}$	0.04	7.1×10^{-10}	0.74
30b		→	$Ph_2CS^{\bullet -} + [CS]$	0.96		
31a	O_2	$\xrightarrow{He}$	$Ph_2CO_2^{\bullet -}$	0.29	4.8×10^{-11}	0.08
31b		→	$PhCO_2^- + [Ph^{\bullet}]$	0.36		
31c		→	$PhO^- + [PhCO^{\bullet}]$	0.21		
31d		→	$Ph^- + [Ph^{\bullet} + CO_2]$	0.10		
31e		→	$O^{\bullet -} + [Ph_2C{=}O]$	0.04		

[a] Although the reproducibility of the rate constants is ≤±7%, the possible systematic uncertainties in calibrations suggest that their accuracy is ±20%. [b] Reaction efficiency = (k_{total}/k_{ADO}), where k_{ADO} is the collision-limited rate constant calculated by the average dipole orientation theory.[23] [c] See text. [d] The collision-limited rate constant was calculated by using Langevin theory.

through two traps filled with Davison 4-Å molecular sieves cooled with liquid nitrogen. The helium was warmed to room temperature in a glass coil prior to introduction into the upstream end of the flow tube. Gas and liquid neutral reactants were obtained from standard commercial sources. Gas reagents were used as received. 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. $Ph_2C{=}N_2$ was prepared by a literature procedure.[5]

Results

The kinetic and product data for the ion–molecule reactions of $Ph_2C^{\bullet -}$ (m/z 166) are summarized in Table I. In all experiments, clean pseudo-first-order decay plots of the log of the ion signal of $Ph_2C^{\bullet -}$ vs [N] were observed. The primary product ion branching fractions given in Table I were the relative product ion signals obtained by integration of the negative ion spectra taken during the kinetic run. These branching fractions did not vary outside of our experimental error (±3%) out to >95% decay of the $Ph_2C^{\bullet -}$ ion signal. Unless otherwise noted, >90% of the decay of the m/z 166 ion was observed as product ion(s) signal intensity.

Discussion

Reactions of $Ph_2C^{\bullet -}$ with Potential Proton Donors—Proton Affinity and $\Delta H_f°$ of $Ph_2C^{\bullet -}$. Once the method of generating a new HNI species was developed, the next task was to bracket its proton affinity (PA) from which the $\Delta H_f°$ of the HNI species could be calculated. With this value available, the thermochemistry of other reactions could then be calculated. The reactions used to bracket PA($Ph_2C^{\bullet -}$) and their results are given in Table II.

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(5) Miller, J. B. *J. Org. Chem.* **1959**, *24*, 560.

Table II. Data for Bracketing PA($Ph_2C^{\bullet -}$) in H^+-Transfer Reactions with HA Acids

HA	product ion	H^+ transfer	$\Delta H_{acid}°$(HA),[a] kcal mol^{-1}
$(CH_3)_2CHOH$	$(CH_3)_2CHO^-$	yes	374.1
HC_2H	HC_2^-	yes	375.4
C_2H_5OH	$C_2H_5O^-$	yes	376.1
$C_6H_5CH(CH_3)_2$	$C_6H_5C(CH_3)_2^-$	yes	377.5
n-$C_3H_7C_2H$	*n*-$C_3H_7C_2^-$	yes	378.3
$C_6H_5CH_3$	$C_6H_5CH_2^-$	yes	379.0
CH_3OH	CH_3O^-	yes	379.2
CH_3C_2H	$CH_3C_2^-$	yes	379.6
p-$CH_3C_6H_4CH_3$		no	380.5
$CH_3CH{=}CH_2$		no	390.8
H_2O		no	390.8

[a] Reference 6; errors are ±2 kcal mol^{-1}.

The fast reaction of $Ph_2C^{\bullet -}$ with acetylene proceeded exclusively by H^+ transfer, yielding the *m*/*z* 25 anion (HC_2^-) (eq 2). A

$$Ph_2C^{\bullet -} + RC_2H \rightarrow Ph_2CH^{\bullet} + RC_2^- \qquad R = H,\ n\text{-}C_3H_7 \quad (2)$$

similar result was observed when *n*-$C_3H_7C_2H$ was used, where *n*-$C_3H_7C_2^-$ was the product anion produced. Proton transfer was also observed between $Ph_2C^{\bullet -}$ and $C_6H_5CH(CH_3)_2$ and $C_6H_5CH_3$; the rate constants were not measured in these reactions due to the high boiling points of these neutrals. The rate constant for H^+ transfer between $Ph_2C^{\bullet -}$ and propyne was 1 order of magnitude less than those with the above two acetylenes, indicating that we were approaching the upper limit for PA($Ph_2C^{\bullet -}$).[3]

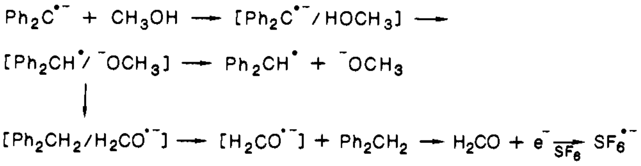
In the bracketing of PA($Ph_2C^{\bullet -}$), several alcohols were also used as the neutral reactants. The fast reaction of $Ph_2C^{\bullet -}$ with $(CH_3)_2CHOH$ ($\Delta H_{acid}°$ = 374.1 kcal mol^{-1})[6] occurred at nearly the collision limit and produced the product ion of H^+ transfer, $(CH_3)_2CHO^-$ (*m*/*z* 61), and its alcohol cluster ions at *m*/*z* 123 and 185 (eq 3). In this reaction, the sum of the product ion signal

$$\underset{m/z\ 166}{Ph_2C^{\bullet -}} + (CH_3)_2CHOH \longrightarrow Ph_2CH^{\bullet} + \underset{m/z\ 61}{(CH_3)_2CHO^-} \xrightarrow{(CH_3)_2CHOH} \underset{m/z\ 123.185}{(CH_3)_2CHO^-((CH_3)_2CHOH)_{1.2}} \quad (3)$$

integrals was 90% of the integrated signal for the decay of the starting *m*/*z* 166 ion. The reaction of $Ph_2C^{\bullet -}$ with C_2H_5OH ($\Delta H_{acid}°$ = 376.1 kcal mol^{-1})[6] proceeded in a similar manner, yielding $C_2H_5O^-$ (*m*/*z* 45) along with the higher cluster ions $C_2H_5O^-(C_2H_5OH)_{1,2}$ (*m*/*z* 91 and 137), but the integrated signals of the product ions only accounted for 65% of the decay of the *m*/*z* 166 ion. The corresponding reaction with CH_3OH ($\Delta H_{acid}°$ = 379.2 kcal mol^{-1})[6] again produced decay of the *m*/*z* 166 ion at nearly the collision limit (Table I), but the integrated signals of the product ions, CH_3O^- (*m*/*z* 31) and $CH_3O^-(CH_3OH)$ (*m*/*z* 63), only represented 5% of the total decay of the $Ph_2C^{\bullet -}$ starting ion.

This loss of observable product ion signal for the reactions involving the weaker acids C_2H_5OH and especially CH_3OH suggested that an additional process was occurring in the initial collision encounter between $Ph_2C^{\bullet -}$ and these alcohols. The absence of observable product ion(s) to account for the complete decay of $Ph_2C^{\bullet -}$ further suggested that electron autodetachment had occurred from a metastable negative ion product. To test this possibility, two experiments were carried out: (i) When SF_6 was added to the flow via an inlet located just downstream of the inlet port where CH_3OH was added, a large signal for $SF_6^{\bullet -}$ was observed, indicating that free electrons were indeed present at this point and further downstream in the flow. (ii) When the gaseous CH_3OH flow through its inlet was discontinued, *no* signal for $SF_6^{\bullet -}$ was observed when SF_6 was added to the flow containing $Ph_2C^{\bullet -}$ and some neutral Ph_2CN_2. These results established that the generation of the electron in experiment i was the direct result of the ion–molecule reaction of $Ph_2C^{\bullet -}$ with CH_3OH, with the product negative ion undergoing electron detachment. Since only the small product ion signals for CH_3O^- (EA($CH_3O^{\bullet}$) = 36 kcal mol^{-1})[7a] and its CH_3OH cluster ions were observed in the original ion–molecule reaction, we rule out electron transfer between some metastable negative ion product and SF_6 (EA = 23 kcal mol^{-1}),[7] yielding $SF_6^{\bullet}$ in experiment i.

Scheme I



To rationalize the present results, we suggest that the unobserved negative ion product was $H_2C{=}O^{\bullet -}$ formed by H atom transfer within the collision complex [$Ph_2CH^{\bullet}$/$^-OCH_3$] formed by initial H^+ transfer. Formaldehyde is known to have a negative EA (−19 kcal mol^{-1}).[8] The series of reactions describing this are shown in Scheme I. The sum of the integrated signals of the $SF_6^{\bullet -}$ ions and those at *m*/*z* 31 and 63 was about 85% of the decay of $Ph_2C^{\bullet -}$ in experiment i above. This approach has the direct analogy in our previous report of a related $H_2^{\bullet +}$ transfer between $(CF_3)_2C^{\bullet -}$ and CH_3SH, forming $H_2CS^{\bullet -}$ (*m*/*z* 46) as an observed minor product;[9] in this case, $H_2C{=}S$ was expected to have a positive EA.[10] We have also observed that the ketyl anion radical $(CF_3)_2CO^{\bullet -}$ was produced exclusively in the $H_2^{\bullet +}$ transfer reaction between $CF_3CH^{\bullet -}$ and $(CF_3)_2CHOH$.[11]

While the $H_2^{\bullet +}$-transfer process was accounted for as the major product-forming channel in the reaction of $Ph_2C^{\bullet -}$ with CH_3OH, the reactions with C_2H_5OH and $(CH_3)_2CHOH$ were also investigated by adding SF_6 downstream of the alcohol inlet port. A significant signal for $SF_6^{\bullet -}$ was observed in the C_2H_5OH reaction, but no $SF_6^{\bullet -}$ ion signal was produced in the $(CH_3)_2CHOH$ reaction. Therefore, the low product negative ion recoveries observed in the reactions of $Ph_2C^{\bullet -}$ with CH_3OH and C_2H_5OH are accounted for.

No reaction was observed between $Ph_2C^{\bullet -}$ and *p*-xylene, propylene, or H_2O; that is $k < 10^{13}$ cm^3 molecule^{-1} s^{-1}. From the data in Table II, we conclude that PA($Ph_2C^{\bullet -}$) = 380 ± 2 kcal mol^{-1}. With use of the reported values $\Delta H_f°(Ph_2CH^{\bullet}) = 69 \pm 2$ kcal mol^{-1} [12] and $\Delta H_f°(H^+)$ = 367.2 kcal mol^{-1} [6] and the relationship $\Delta H_f°(Ph_2C^{\bullet -}) = \Delta H_f°(Ph_2CH^{\bullet}) - \Delta H_f°(H^+) +$ PA($Ph_2C^{\bullet -}$), $\Delta H_f°(Ph_2C^{\bullet -}) = 81.8 \pm 2$ kcal mol^{-1} was calculated. On the basis of this value, we calculate that the $H_2^{\bullet +}$-transfer reactions between $Ph_2C^{\bullet -}$ and the alcohols producing Ph_2CH_2, the corresponding carbonyl compound, and the electron have exothermicities of 20 (with CH_3OH), 26 (with C_2H_5OH), and 29 kcal mol^{-1} (with $(CH_3)_2CHOH$). The increasing exothermicity of H^+ transfer with $(CH_3)_2CHOH$, and to some extent with C_2H_5OH, appears to effect separation of the partners of the H^+-transfer complex, and the further transfer of the H atom is limited.

Reactions of $Ph_2C^{\bullet -}$ with Alkyl Halides and Other CH_3X Molecules—S_N2 Nucleophilicity of $Ph_2C^{\bullet -}$. $Ph_2C^{\bullet -}$ reacted rapidly with CH_3Br to yield Br^- exclusively. The analogous reaction with

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(6) (a) Bartmess, J. E.; McIver, R. T. In *Gas Phase Ion Chemistry*; Bowers, M. T., Ed.; Academic: New York, 1979; Vol. 2, Chapter 11. (b) Moylan and Brauman suggested that the $\Delta H_{acid}°$(ROH) values between 371.8 and 379.2 kcal mol^{-1} [6a] be increased by about 2 kcal mol^{-1}: Moylan, C. R.; Brauman, J. I. *J. Phys. Chem.* **1984**, *88*, 3175. In the present study, we have used the original values given in ref 6a.

(7) (a) Drzaic, P. S.; Marks, J.; Brauman, J. I. In *Gas Phase Ion Chemistry*; Bowers, M. T., Ed.; Academic: New York, 1984; Vol. 3, Chapter 21. (b) Streit, G. E. *J. Chem. Phys.* **1982**, *77*, 826.

(8) Jordan, K. D.; Burrow, P. D. *Acc. Chem. Res.* **1978**, *11*, 341.

(9) McDonald, R. N.; Chowdhury, A. K.; McGhee, W. D. *J. Am. Chem. Soc.* **1984**, *106*, 4112.

(10) Professors K. D. Jordan and P. D. Burrow (private communication) have estimated that $H_2C{=}S$ should have a positive EA.

(11) McDonald, R. N.; McGhee, W. D.; Chowdhury, A. K., unpublished results.

(12) Rossi, M. J.; McMillen, D. F.; Golden, D. M. *J. Phys. Chem.* **1984**, *88*, 5031.

$\mathrm{CH_3Cl}$ yielding $\mathrm{Cl^-}$ occurred with a rate constant 1 order of magnitude smaller than that measured for the $\mathrm{CH_3Br}$ reaction (eq 4). On the basis of Bohme's kinetic nucleophilicity scale,[13]

$$\mathrm{Ph_2C^{\bullet-} + CH_3X \rightarrow CH_3X \rightarrow Ph_2C(CH_3)^{\bullet} + X^-} \qquad (4)$$

$\mathrm{Ph_2C^{\bullet-}}$ must be considered to be at the lower end for those anions exhibiting *medium* $\mathrm{S_N2}$ nucleophilicity. This is in spite of the large exothermicity for the reaction with $\mathrm{CH_3Cl}$ ($\Delta H° = -55$ kcal $\mathrm{mol^{-1}}$),[14] which is reflected in the large methyl cation affinity of $\mathrm{Ph_2C^{\bullet-}}$ (283 kcal $\mathrm{mol^{-1}}$).[16] These kinetic and thermochemical data suggest that a significant intrinsic barrier exists in these $\mathrm{S_N2}$ displacement reactions, which are only partially compensated for by the large reaction exothermicity.[17]

On the basis of the above conclusion, it was of interest to examine the reactions of $\mathrm{Ph_2C^{\bullet-}}$ with several methyl esters to determine whether carbonyl addition, followed by radical β-fragmentation (shown in eq 1 with $\mathrm{PhN^{\bullet-}}$), would be competitive with the $\mathrm{S_N2}$ reaction channel. Indeed, this was observed. The reaction of $\mathrm{Ph_2C^{\bullet-}}$ with $\mathrm{CF_3CO_2CH_3}$ occurred at nearly the collision limit with only a small contribution (5%) from the highly exothermic (−70 kcal $\mathrm{mol^{-1}}$)[18] $\mathrm{S_N2}$ channel, yielding $\mathrm{CF_3CO_2^-}$. The fast reactions of $\mathrm{Ph_2C^{\bullet-}}$ with $\mathrm{HCO_2CH_3}$ and $\mathrm{CH_3CO_2CH_3}$ occurred exclusively by reaction channels other than that of $\mathrm{S_N2}$ displacement. These results were self-consistent in that $\mathrm{CF_3CO_2^-}$ is a much better anionic leaving group than either $\mathrm{HCO_2^-}$ or $\mathrm{CH_3CO_2^-}$ in displacement reactions. The details of the results of the reactions with these esters will be presented in a later section.

In the condensed phase, $\mathrm{CH_3X}$ molecules were found to react 30 times faster, on the average, than the $\mathrm{C_2H_5X}$ derivatives in $\mathrm{S_N2}$ displacement reactions.[19] The reaction of $\mathrm{Ph_2C^{\bullet-}}$ with $\mathrm{C_2H_5Br}$ yielding $\mathrm{Br^-}$ occurred with a rate constant 3 times smaller than that measured for the reaction with $\mathrm{CH_3Br}$. However, since both rate constants were close to the collision limits, this comparison is poor at best. A better comparison of this alkyl group effect is seen in the slower reactions with $\mathrm{CH_3Cl}$ and $\mathrm{C_2H_5Cl}$. Here the ratio of $k_{\mathrm{CH_3Cl}}/k_{\mathrm{C_2H_5Cl}} = 23$, in excellent agreement with Streitwieser's average value of 30 in related condensed-phase reactions[19] and similar ratios observed previously for reactions of $\mathrm{PhN^{\bullet-}}$ in the gas phase.[1] However, we cannot rule out an E2 elimination component in the reactions of the strongly basic $\mathrm{Ph_2C^{\bullet-}}$ with $\mathrm{C_2H_5Br}$ and $\mathrm{C_2H_5Cl}$.

Reactions of $\mathrm{Ph_2C^{\bullet-}}$ with Carbonyl-Containing Organic Molecules. a. Aldehydes. The reactions of $\mathrm{Ph_2C^{\bullet-}}$ with three aldehydes, $\mathrm{CH_3CHO}$, $\mathrm{C_2H_5CHO}$, and $\mathrm{(CH_3)_3CCHO}$, were examined. With the former two aldehydes, $\mathrm{H^+}$ transfer was competitive with the channel of carbonyl addition/radical β-fragmentation because $\mathrm{Ph_2C^{\bullet-}}$ is a strong base. In the reaction of $\mathrm{Ph_2C^{\bullet-}}$ with $\mathrm{CH_3CHO}$, two product ions at m/z 43 and 195 were formed, which were assigned the structures of the enolate anions shown in eq 5. The

$$\underset{m/z\ 166}{\mathrm{Ph_2C^{\bullet-}}} + \mathrm{CH_3CHO} \xrightarrow{0.50} \underset{m/z\ 195}{\mathrm{Ph_2C{=}C(O^-)H}} + \mathrm{{}^{\bullet}CH_3} \qquad (5a)$$

$$\xrightarrow{0.50} \underset{m/z\ 43}{\mathrm{CH_2{=}C(O^-)H}} + \mathrm{Ph_2CH^{\bullet}} \qquad (5b)$$

related ion products from the reaction of $\mathrm{Ph_2C^{\bullet-}}$ with $\mathrm{C_2H_5CHO}$ at m/z 57 and 195 were assigned the structures of the corresponding enolate anions shown in eq 6. In the reaction of $\mathrm{Ph_2C^{\bullet-}}$

$$\underset{m/z\ 166}{\mathrm{Ph_2C^{\bullet-}}} + \mathrm{C_2H_5CHO} \xrightarrow{0.54} \underset{m/z\ 195}{\mathrm{Ph_2C{=}C(O^-)H}} + \mathrm{C_2H_5^{\bullet}} \qquad (6a)$$

$$\xrightarrow{0.46} \underset{m/z\ 57}{\mathrm{CH_3CH{=}C(O^-)H}} + \mathrm{Ph_2CH^{\bullet}} \qquad (6b)$$

with $\mathrm{(CH_3)_3CCHO}$, the absence of a $\mathrm{C_\alpha{-}H}$ bond in the aldehyde removed the possibility of simple $\mathrm{H^+}$ transfer and only the product of carbonyl addition/radical β-fragmentation was observed (eq 7). It is interesting in these three reactions that the only product

$$\underset{m/z\ 166}{\mathrm{Ph_2C^{\bullet-}}} + \mathrm{(CH_3)_3CCHO} \rightarrow \underset{m/z\ 195}{\mathrm{Ph_2C{=}C(O^-)H}} + \mathrm{(CH_3)_3C^{\bullet}} \qquad (7)$$

of carbonyl addition/radical β-fragmentation was that of alkyl radical cleavage. This is not surprising since the alternate cleavage of an H atom from the tetrahedral anion radical intermediate should be less exothermic.

A third possible primary reaction channel, that of H atom abstraction by $\mathrm{Ph_2C^{\bullet-}}$ from RCHO, was not observed. This H atom transfer should be reasonably exothermic since $D°(\mathrm{Ph_2C^-{-}H}) = 99 \pm 4$ kcal $\mathrm{mol^{-1}}$,[20] while $D°(\mathrm{RC({=}O)H}) \approx 87$ kcal $\mathrm{mol^{-1}}$.[15] Since the three reactions of $\mathrm{Ph_2C^{\bullet-}}$ with these aldehydes are fast (reaction efficiencies >0.50) and must proceed to the tetrahedral intermediate and/or suffer $\mathrm{H^+}$ transfer with low barriers in the collision complexes $\mathrm{[Ph_2C^{\bullet-}/RCHO]}$, the absence of H atom transfer means that a much larger barrier exists for the H atom abstraction channel compared to the ionic reaction channels.

b. Ketones. The fast reaction of $\mathrm{Ph_2C^{\bullet-}}$ with $\mathrm{CF_3C({=}O)CH_3}$ occurred at unit efficiency and exclusively formed the enolate anion $\mathrm{CF_3C(O^-){=}CH_2}$ (m/z 111) (eq 8). Formation of this product ion was expected due to the acidity of this ketone ($\Delta H_{\mathrm{acid}}° = 350.3$ kcal $\mathrm{mol^{-1}}$),[6] and the $\mathrm{H^+}$-transfer channel was 32 kcal $\mathrm{mol^{-1}}$ (exothermic).

$$\underset{m/z\ 166}{\mathrm{Ph_2C^{\bullet-}}} + \mathrm{CF_3C({=}O)CH_3} \rightarrow \mathrm{Ph_2CH^{\bullet}} + \underset{m/z\ 111}{\mathrm{CF_3C(O^-){=}CH_2}} \qquad (8)$$

$\mathrm{Ph_2C^{\bullet-}}$ reacted almost as rapidly with $\mathrm{(CH_3)_2C{=}O}$ ($\Delta H_{\mathrm{acid}}° = 368.8$ kcal $\mathrm{mol^{-1}}$)[6] by major $\mathrm{H^+}$ transfer and minor carbonyl addition/radical β-fragmentation, yielding the two enolate anions shown in eq 9. In the related reaction of $\mathrm{Ph_2C^{\bullet-}}$ with the α-diketone biacetyl, analogous product enolate negative ions were observed (eq 10). In both of these reactions, $\mathrm{H^+}$ transfer and

$$\underset{m/z\ 166}{\mathrm{Ph_2C^{\bullet-}}} + \mathrm{(CH_3)_2C{=}O} \xrightarrow{0.90} \mathrm{Ph_2CH^{\bullet}} + \underset{m/z\ 57}{\mathrm{CH_2{=}C(O^-)CH_3}} \qquad (9a)$$

$$\xrightarrow{0.10} \underset{m/z\ 209}{\mathrm{Ph_2C{=}C(O^-)CH_3}} + \mathrm{{}^{\bullet}CH_3} \qquad (9b)$$

$$\underset{m/z\ 166}{\mathrm{Ph_2C^{\bullet-}}} + \mathrm{CH_3COCOCH_3} \xrightarrow{0.77} \mathrm{Ph_2CH^{\bullet}} + \underset{m/z\ 85}{\mathrm{CH_2{=}C(O^-)COCH_3}} \qquad (10a)$$

$$\xrightarrow{0.23} \underset{m/z\ 209}{\mathrm{Ph_2C{=}C(O^-)CH_3}} + \mathrm{CH_3C({=}O)^{\bullet}} \qquad (10b)$$

carbonyl addition/radical β-fragmentation are competitive channels. In the analogous reaction of $\mathrm{PhN^{\bullet-}}$ with biacetyl, 98% of the reaction occurred by the addition/fragmentation mechanism and only 2% by $\mathrm{H^+}$ transfer.[1]

c. Esters. The reactions of $\mathrm{Ph_2C^{\bullet-}}$ with esters are interesting because the stage is set for a direct comparison of two different nucleophilic mechanisms, (a) carbonyl addition/radical β-fragmentation and (b) $\mathrm{S_N2}$ displacement at $\mathrm{C_\alpha}$ of the ethereal alkyl group (E2 elimination is also possible with alkyl groups larger than $\mathrm{CH_3}$). As mentioned above, the *medium* kinetic nucleophilicity of $\mathrm{Ph_2C^{\bullet-}}$ in $\mathrm{S_N2}$ reactions rules out this as a competing

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(13) Tanaka, K.; MacKay, G. I.; Payzant, J. D.; Bohme, D. K. *Can. J. Chem.* **1976**, *54*, 1643.

(14) $\Delta H_f°(\mathrm{Ph_2C(CH_3)^{\bullet}}) = 60.9$ kcal $\mathrm{mol^{-1}}$;[11] $\Delta H_f°(\mathrm{CH_3Cl}) = -20.6$ kcal $\mathrm{mol^{-1}}$;[15] $\Delta H_f°(\mathrm{Cl^-}) = -54.4$ kcal $\mathrm{mol^{-1}}$ (based on $\Delta H_f°(\mathrm{Cl^{\bullet}})$[15] and EA($\mathrm{Cl^{\bullet}}$)).[7]

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

(16) $\Delta H_f°(\mathrm{CH_3^+}) = 262$ kcal $\mathrm{mol^{-1}}$: Rosenstock, H. M.; Draxl, K.; Steiner, B. W.; Herron, J. T. *J. Phys. Chem. Ref. Data, Suppl. 1*, **1977**, *6*.

(17) Pellerite, M. J.; Brauman, J. I. *J. Am. Chem. Soc.* **1983**, *105*, 2672.

(18) $\Delta H_f°(\mathrm{CF_3CO_2CH_3}) = -240.7$ kcal $\mathrm{mol^{-1}}$; $\Delta H_f°(\mathrm{CF_3CO_2^-}) = -290$ kcal $\mathrm{mol^{-1}}$.[6]

(19) Streitwieser, A. *Solvolytic Displacement Reactions*; McGraw-Hill: New York, 1962; pp 11–13.

(20) $\Delta H_f°(\mathrm{Ph_2CH^-}) = 37$ kcal $\mathrm{mol^{-1}}$.[6]

reaction with most ester molecules.

The reaction of $Ph_2C^{\bullet-}$ with HCO_2CH_3 was of special interest to us since the large PA($Ph_2C^{\bullet-}$) opened up the possibility of an additional reaction channel, that of the Riveros reaction.[21] In the Riveros reaction, the basic negative ion is thought to abstract the formyl proton followed by decarbonylation yielding CH_3O^- ion. However, in this case, the Riveros reaction is *endothermic* by 8.4 kcal mol^{-1},[12,22] and reaction could not be observed under these experimental conditions. The result of the fast reaction of $Ph_2C^{\bullet-}$ with HCO_2CH_3 was exclusive formation of the *m/z* 195 ion believed to be the enolate anion shown in eq 11 formed by the carbonyl addition/radical β-fragmentation mechanism.

$$\underset{m/z\ 166}{Ph_2C^{\bullet-}} + HCO_2CH_3 \rightarrow \underset{m/z\ 195}{Ph_2C{=}C(O^-)H} + {}^{\bullet}OCH_3 \tag{11}$$

The excellent recovery (>95%) of the product ion at *m/z* 195 in this reaction compared to the decay of the *m/z* 166 ion demonstrated that the Riveros reaction and S_N2 displacement were absent. Comparison of the results of the reactions of $Ph_2C^{\bullet-}$ and $PhN^{\bullet-}$ with HCO_2CH_3 (for $PhN^{\bullet-}$, $k^{C{=}O} = 1.3 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1}),[1] we see that $Ph_2C^{\bullet-}$ is more reactive than $PhN^{\bullet-}$ in carbonyl addition with this ester by a factor of 120.

The fast reaction of $Ph_2C^{\bullet-}$ with $CH_3CO_2CH_3$ occurred at 10% of the collision limit, k_{ADO}[23] (eq 12). However, the major reaction

$$\underset{m/z\ 166}{Ph_2O^{\bullet-}} + CH_3CO_2CH_3 \xrightarrow{0.97} Ph_2CH^{\bullet} + \underset{m/z\ 73}{CH_2{=}C(O^-)OCH_3} \tag{12a}$$

$$\xrightarrow{0.03} \underset{m/z\ 209}{Ph_2C{=}C(O^-)CH_3} + CH_3O^{\bullet} \tag{12b}$$

channel was that of H^+ transfer (eq 12a), with only a small amount of the enolate anion at *m/z* 209 formed by carbonyl addition/radical β-fragmentation. Obviously, more than acidity is involved here since $CH_3CO_2CH_3$ ($\Delta H_{acid}{}^{\circ}$ = 371 kcal mol^{-1})[6] is 4.6 kcal mol^{-1} *less* acidic than CH_3CHO, which gave equal amounts of products generated by the same two mechanisms. We interpret these results as showing that the aldehyde carbonyl is *more* reactive than the ester carbonyl with $Ph_2C^{\bullet-}$. This is also seen in their absolute rate constants even though both are close to the collision limit. If we factor k_{total} for this reaction with $CH_3CO_2CH_3$ into its components for H^+ transfer and carbonyl addition, we find that $k^{C{=}O} = 8.9 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1}; however, since k_{total} is near the collision limit, this $k^{C{=}O}$ is a minimum value. When this is compared to $k^{C{=}O}$ for the reaction of $PhN^{\bullet-}$ with $CH_3CO_2CH_3$ (1.3×10^{-13} cm^3 molecule^{-1} s^{-1}), we conclude that $Ph_2C^{\bullet-}$ is the better nucleophile toward carbonyl addition with $CH_3CO_2CH_3$ by a factor of >30.

The fast reaction of $Ph_2C^{\bullet-}$ with $CF_3CO_2CH_3$ proceeded at 71% of the collision limit and formed the three product anions shown in eq 13. The two enolate anions at *m/z* 225 and 263 are believed

$$\underset{m/z\ 166}{Ph_2C^{\bullet-}} + CF_3CO_2CH_3 \xrightarrow{0.81} \underset{m/z\ 263}{Ph_2C{=}C(O^-)CF_3} + CH_3O^{\bullet} \tag{13a}$$

$$\xrightarrow{0.14} \underset{m/z\ 225}{Ph_2C{=}C(O^-)OCH_3} + {}^{\bullet}CF_3 \tag{13b}$$

$$\xrightarrow{0.05} \underset{m/z\ 113}{CF_3CO_2^-} + Ph_2C(CH_3)^{\bullet} \tag{13c}$$

to be produced by carbonyl addition, forming the excited tetrahedral intermediate [$Ph_2\dot{C}C(O^-)(CF_3)(OCH_3)$] followed by radical β-fragmentation and competitive loss of ${}^{\bullet}CF_3$ and ${}^{\bullet}OCH_3$. Formation of $CF_3CO_2^-$ at *m/z* 113 is most reasonably accounted for by S_N2 displacement. The analogous reaction with the ethyl ester, $CF_3CO_2C_2H_5$, produced only the products of carbonyl addition/radical β-fragmentation (eq 14) in a ratio similar to those

$$\underset{m/z\ 166}{Ph_2C^{\bullet-}} + CF_3CO_2C_2H_5 \xrightarrow{0.90} \underset{m/z\ 263}{Ph_2C{=}C(O^-)CF_3} + C_2H_5O^{\bullet} \tag{14a}$$

$$\xrightarrow{0.10} \underset{m/z239}{Ph_2C{=}C(O^-)OC_2H_5} + {}^{\bullet}CF_3 \tag{14b}$$

observed in eq 13a and 13b for the methyl ester. As was mentioned earlier, S_N2 displacement and/or E2 elimination reactions with ethyl derivatives are slower than those with the corresponding methyl derivatives, which accounts for the absence of $CF_3CO_2^-$ (*m/z* 113) in reaction 14.

The fast reaction of $Ph_2C^{\bullet-}$ with the thioester $CF_3C({=}O)SC_2H_5$ produced a surprise in the formation of an anion with the elemental formula of the conjugate base of the ester at *m/z* 157 as a minor product (eq 15). The two major product negative ions at *m/z* 129 and 263 appear to be the result of S_N2 displacement and carbonyl addition/radical β-fragmentation mechanisms, respectively. The structure of the unusual anion at *m/z* 157 is unknown; the presence of one sulfur and four carbons was verified by the magnitudes of the (M + 1) and (M + 2) isotope peaks in the *m/z* 157 ion. One possible structure for this ion is $CF_3C({=}O)C_2H_4S^-$ formed by initial H^+ abstraction of a C_β–H from the ester followed by rearrangement. This rearrangement could have been competitive with elimination of CF_3COS^- observed in eq 15b. However, it is not clear why similar H^+ abstraction did not occur in the reaction with the ethyl ester in eq 14 and produce $CF_3CO_2^-$.

$$\underset{m/z\ 166}{Ph_2C^{\bullet-}} + CF_3C({=}O)SC_2H_5 \xrightarrow{0.45} \underset{m/z\ 263}{Ph_2C{=}C(O^-)CF_3} + C_2H_5S^{\bullet} \tag{15a}$$

$$\xrightarrow{0.45} \underset{m/z\ 129}{CF_3COS^-} + Ph_2C(C_2H_5)^{\bullet} \tag{15b}$$

$$\xrightarrow{0.10} \underset{m/z\ 157}{CF_3COSC_2H_4^-} + Ph_2CH^{\bullet} \tag{15c}$$

The reaction of $Ph_2C^{\bullet-}$ with methyl pyruvate was examined since this neutral reactant offers an intramolecular comparison of a keto and an ester carbonyl group. With $PhN^{\bullet-}$, this ester exhibited 7 times greater carbonyl addition/radical β-fragmentation reactivity at the keto carbonyl than at the ester carbonyl group. The results of the reaction are shown in eq 16. As expected from the results obtained with $CH_3CO_2CH_3$, H^+ transfer was an important product-forming channel. The product ion at *m/z* 209 (eq 16b) is considered to be generated by initial nucleophilic addition of $Ph_2C^{\bullet-}$ to the keto carbonyl of the ester forming **1** followed by radical β-fragmentation with loss of ${}^{\bullet}CO_2CH_3$ radical or its equivalent. The product ions at *m/z* 225 and 237 (eq 16c and 16d) are consistent with the initial nucleo-

$$\underset{m/z\ 166}{Ph_2C^{\bullet-}} + CH_3COCO_2CH_3 \xrightarrow{0.33} \underset{m/z\ 101}{CH_2{=}C(O^-)CO_2CH_3} + Ph_2CH^{\bullet} \tag{16a}$$

$$\xrightarrow{0.54} \underset{m/z\ 209}{Ph_2C{=}C(O^-)CH_3} + {}^{\bullet}CO_2CH_3 \tag{16b}$$

$$\xrightarrow{0.08} \underset{m/z237}{Ph_2C{=}C(O^-)COCH_3} + {}^{\bullet}OCH_3 \tag{16c}$$

$$\xrightarrow{0.05} \underset{m/z\ 225}{Ph_2C{=}C(O^-)OCH_3} + CH_3CO^{\bullet} \tag{16d}$$

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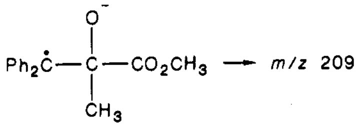
[21] (a) Faigle, J. F. G.; Isolani, P. C.; Riveros, J. M. *J. Am. Chem. Soc.* **1976**, *98*, 2049. (b) Isolani, P. C.; Riveros, J. M. *Chem. Phys. Lett.* **1975**, *33*, 362. (c) Blair, L. K.; Isolani, P. C.; Riveros, J. M. *J. Am. Chem. Soc.* **1973**, *95*, 1057.

[22] $\Delta H_f{}^{\circ}(HCO_2CH_3) = -83.6$ kcal mol^{-1};[15] $\Delta H_f{}^{\circ}(CO) = -26.4$ kcal mol^{-1};[15] $\Delta H_f{}^{\circ}(CH_3O^-) = -36$ kcal mol^{-1}.[6]

[23] Collision-limited rate constants are calculated by the average dipole orientation (ADO) theory: Su, T.; Bowers, M. T. In *Gas Phase Ion Chemistry*; Bowers, M. T., Ed.; Academic: New York, 1979; Vol. 1, Chapter 3.



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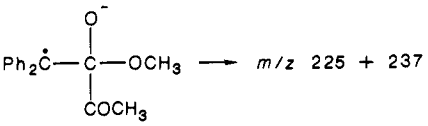

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philic addition occurring at the ester carbonyl group followed by competitive radical β-fragmentation with loss of $^{\bullet}OCH_3$ and $CH_3CO^{\bullet}$, respectively. On the basis of these data, the keto carbonyl in methyl pyruvate is more reactive than the ester carbonyl toward nucleophilic attack by $Ph_2C^{\bullet-}$ by a factor of 4.2.

d. Relative Reactivities of $Ph_2C^{\bullet-}$ with Carbonyl-Containing Organic Molecules. It is difficult to determine the relative reactivities of $Ph_2C^{\bullet-}$ with the aldehydes, ketones, and esters used in this study since all of the rate constants were >10% of the collision limit. However, the result with methyl pyruvate showed that the keto carbonyl was 4.2 times more reactive than the carbomethoxy carbonyl in the intramolecular test molecule. This compared favorably with the value of 7 observed for this ratio in the reaction of this α-keto ester with $PhN^{\bullet-}$.[1] On the basis of this result and other discussion previously given, it seems reasonable to conclude that the reactivity of $Ph_2C^{\bullet-}$ with carbonyl centers parallels that of $PhN^{\bullet-}$, however, with much larger rate constants. On the basis of this premise and the present data, it should now be possible to compare the reactivities of several carbonyl-containing functional groups that react slower than the simple ester molecule $CH_3CO_2CH_3$. Obviously, H^+ transfer will remain as a potentially important product-forming channel if it can occur.

Reactions of $Ph_2C^{\bullet-}$ with CO_2, COS, CS_2, and O_2. In the reactions of $Ph_2C^{\bullet-}$ with these four neutrals, we observed formation of a total adduct. To observe such adducts, we assume that the initially formed excited adduct must undergo collisional stabilization with the helium buffer gas to remove sufficient excess vibrational energy or the adducts will decompose. $Ph_2C^{\bullet-}$ reacted rapidly with CO_2 to form the total adduct (m/z 210) and a trace of the apparent produced of O atom transfer at m/z 182 (eq 17).

$$\underset{m/z\ 166}{Ph_2C^{\bullet-}} + CO_2 \xrightarrow[He]{0.99} \underset{m/z\ 210}{Ph_2\dot{C}CO_2^-} \tag{17a}$$

$$\xrightarrow{0.01} \underset{m/z\ 182}{Ph_2CO^{\bullet-}} \tag{17b}$$

The reported $EA(Ph_2C{=}O) = 14.6$ kcal mol^{-1} [24] means that the overall O atom transfer from CO_2 to $Ph_2C^{\bullet-}$ is 14.2 kcal mol^{-1} exothermic.[22,25] Oxygen atom transfers from such a stable molecule as CO_2 are not usual happenings. The reaction between $Ph_2C^{\bullet-}$ and COS followed a similar pattern, with adduct formation as the major channel and S atom transfer as the minor channel (eq 18). The observation of a larger amount of S atom transfer

$$\underset{m/z\ 166}{Ph_2C^{\bullet-}} + COS \xrightarrow[He]{0.85} \underset{m/z\ 226}{Ph_2\dot{C}COS^-} \tag{18a}$$

$$\xrightarrow{0.15} \underset{m/z\ 198}{Ph_2CS^{\bullet-}} + CO \tag{18b}$$

in reaction 18 compared to the O atom transfer in reaction 17 is not surprising since $D°(OC{=}S) < D°(OC{=}O)$ by 54 ± 1 kcal mol^{-1}.[27] The product ion ratio, adduct/$Ph_2CS^{\bullet-}$, inverted when CS_2 was allowed to react with $Ph_2C^{\bullet-}$ (eq 19). This is the result of the lower $D°(SC{=}S)$ compared to $D°(OC{=}S)$ by 13 kcal mol^{-1}.[27]

Table III. Thermodynamic Data Obtained in This Study at 298 K[a]

$PA(Ph_2C^{\bullet-}) = 380 \pm 2$

$\Delta H_f°(Ph_2C^{\bullet-}) = 81.8 \pm 2$

$D°(Ph_2C^{-}{-}H) = 96.9 \pm 2$

[a] Data are in kilocalories per mole.

$$\underset{m/z\ 166}{Ph_2C} + CS_2 \xrightarrow[He]{0.04} \underset{m/z\ 242}{Ph_2\dot{C}CS_2^-} \tag{19a}$$

$$\xrightarrow{0.96} \underset{m/z\ 198}{Ph_2CS^{\bullet-}} + CS \tag{19b}$$

Formation of the product ions of O and S atom transfer appear to show that $Ph_2C^{\bullet-}$ can attack two separate sites in these neutral molecules: at the carbon to yield the adducts following collisional stabilization with the helium buffer gas and at the terminal oxygen or sulfur to yield the corresponding terminal atom transfer product. Reactions 17–19 showed no helium pressure effect on the rate constants and branching fractions as P_{He} was varied from 0.5 to 1.0 Torr. These observations are inconsistent with a mechanism of sole attack at carbon, giving the adduct, followed by rearrangement to yield the products of O or S atom transfer where helium buffer gas collisional stabilization and rearrangement were competitive. Generation of the increasing quantities of $Ph_2CS^{\bullet-}$ in reactions 18 and 19 are believed due to decreasing $D°(C{=}S)$ energies in the neutral reactants.[27]

The reaction of $Ph_2C^{\bullet-}$ with O_2 produced five product ions at m/z 198 ($Ph_2CO_2^{\bullet-}$, 29%), 121 ($PhCO_2^-$, 36%), 93 (PhO^-, 21%), 77 (Ph^-, 10%), and 16 (O^-, 4%) covering the range of oxidative fragmentation of $Ph_2C^{\bullet-}$ except for $Ph_2CO^{\bullet-}$. Doubling the P_{He} from 0.5 to 1.0 Torr produced no changes in either the rate constant or the product distribution outside of experimental error.

Summary of Results

$Ph_2C^{\bullet-}$ was generated by dissociative electron attachment to Ph_2CN_2. With use of the bracketing method, $PA(Ph_2C^{\bullet-}) = 380 \pm 2$ kcal mol^{-1} was determined from which the thermodynamic data in Table III were calculated. The large PA of $Ph_2C^{\bullet-}$ is equal to that of CH_3O^- (379.2 ± 2 kcal mol^{-1})[6] and 15.5 kcal mol^{-1} greater than that of the related carbanion Ph_2CH^- (PA = 364.5 kcal mol^{-1}).[6] This larger basicity of the HNI species compared to the corresponding carbanion was also observed with the carbene anion radical c-$C_5H_4^{\bullet-}$ and the anion c-$C_5H_5^-$ where the ΔPA = 21 kcal mol^{-1},[4a] and to a lesser extent with $PhN^{\bullet-}$ vs $PhNH^-$ (ΔPA = 5 kcal mol^{-1})[2] and $(CF_3)_2C^{\bullet-}$ vs $(CF_3)_2CH^-$ (ΔPA = 1 kcal mol^{-1}).[9] In the present case, the large difference in the PAs of $Ph_2C^{\bullet-}$ and Ph_2CH^- is due to the $\Delta H°$s of their separate protonation reactions, $\Delta H_f°(Ph_2CH^{\bullet}) - \Delta H_f°(Ph_2C^{\bullet-}) \approx -13$ kcal mol^{-1} and $\Delta H_f°(Ph_2CH_2) - \Delta H_f°(Ph_2CH^-) \approx +3$ kcal mol^{-1}.

While the reactions of $Ph_2C^{\bullet-}$ with CH_3OH and C_2H_5OH exclusively formed the corresponding alkoxide ions by H^+ transfer, these negative ions signals represented only 5% and 65%, respectively, of the decay of the signal of $Ph_2C^{\bullet-}$. It was demonstrated that the initially "invisible" reaction involved generation of a product ion, which underwent autodetachment of an electron. The presence of the free electron was detected by adding SF_6 to the flow and observing formation of $SF_6^{\bullet-}$. The unobserved metastable intermediates formed in these two reactions were considered to be $H_2CO^{\bullet-}$ and $CH_3CHO^{\bullet-}$, respectively, produced by $H_2^{\bullet+}$ transfer between the reactants.

Although $Ph_2C^{\bullet-}$ shows only medium nucleophilicity in S_N2 reactions with CH_3X molecules, the carbene anion radical is judged to be an excellent nucleophile in carbonyl addition reactions with aldehydes, ketones, and esters. Only in the reactions of $Ph_2C^{\bullet-}$ with CO_2, COS, and CS_2 where O or S atom transfer products

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(25) $\Delta H_f°(CO_2) = -94$ kcal mol^{-1}; $\Delta H_f°(Ph_2C{=}O) = 14.6$ kcal mol^{-1}.[26]

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(27) Dissociation energies calculated from the $\Delta H_f°$s of CO_2, COS, CS_2, CO, CS, O, and S listed in: "JANAF Thermochemical Tables", *Natl. Stand. Ref. Data Ser.* (*U.S., Natl. Bur. Stand.*) **1971**, *No. 37*.

were observed do we see a hint of the carbene anion radical possibly functioning as a free radical.

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Registry No. $Ph_2C^{\bullet -}$, 62268-73-9; HC_2H, 74-86-2; *n*-$C_3H_7C_2H$, 627-19-0; CH_3C_2H, 74-99-7; $(CH_3)_2CHOH$, 67-63-0; C_2H_5OH, 64-17-5; CH_3OH, 67-56-1; $C_6H_5CH(CH_3)_2$, 98-82-8; $C_6H_5CH_3$, 108-88-3; *p*-$CH_3C_6H_4CH_3$, 106-42-3; $CH_3CH{=}CH_2$, 115-07-1; H_2O, 7732-18-5; CH_3Br, 74-83-9; CH_3Cl, 74-87-3; C_2H_5Br, 74-96-4; C_2H_5Cl, 75-00-3; CH_3CHO, 75-07-0; C_2H_5CHO, 123-38-6; $(CH_3)_3CCHO$, 630-19-3; CH_3COCH_3, 67-64-1; CF_3COCH_3, 421-50-1; $CH_3COCOCH_3$, 431-03-8; $CH_3CO_2CH_3$, 79-20-9; HCO_2CH_3, 107-31-3; $CF_3CO_2CH_3$, 431-47-0; $CF_3CO_2C_2H_5$, 383-63-1; $CF_3COSC_2H_5$, 383-64-2; $CH_3COCO_2CH_3$, 600-22-6; CO_2, 124-38-9; CO_5, 463-58-1; CS_2, 75-15-0; O_2, 7782-44-7.

ROH Molecule Assisted Elimination of F^- from $(CF_3)_2CH^-$ and $(CF_3)_2CD^-$ in Gas-Phase E1cb-Type Reactions

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Abstract: The gas-phase reactions of the carbanion $(CF_3)_2CH^-$ with the following series of ROH molecules, $(CF_3)_2CHOH$, CF_3CH_2OH, $(CH_3)_3COH$, CH_3OH, and H_2O, are described. In each case, formation of ROH assisted E1cb elimination cluster ion $F^-(HOR)_x$ ($x \geq 1$) was the major or exclusive reaction channel. The reactions of $(CF_3)_2CD^-$ with these ROH molecules were also examined to observe if D/H exchange occurred in the carbanion–HOR collisions and if deuterium was incorporated into the cluster ion of ROH assisted E1cb elimination. The results from the reactions of $(CF_3)_2CH^-$ and $(CF_3)_2CD^-$ with $(CH_3)_3COH$ [(i) the primary product ion was $F^-(HOC(CH_3)_3)_2$; (ii) extensive D/H exchange was observed in $(CF_3)_2CD^-$, but no deuterium was observed in the fluoride cluster ion product; and (iii) D/H exchange and elimination occurred with the same rate constants] led to the proposal that coordination of $(CH_3)_3COH$ occurred at two separate sites in the carbanion, C_2 for D/H exchange and fluorine of a CF_3 group for the ROH assisted E1cb elimination. The results from the collision limited reactions of $(CF_3)_2CHOH$ and CF_3CH_2OH are consistent with this mechanistic proposal. The reactions of the carbanions with CH_3OH and H_2O were too slow to allow for detailed analysis.

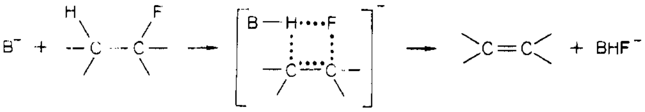
In our reported studies of the generation and thermochemistry of the carbene anion radical $(CF_3)_2C^{\bullet -}$ and the corresponding carbanion $(CF_3)_2CH^-$, the proton affinity of $(CF_3)_2CH^-$ (PA = 364 ± 2 kcal mol^{-1} = $\Delta H^\circ_{acid}((CF_3)_2CH_2)$) was determined with the bracketing method.[1] However, in several reactions of $(CF_3)_2CH^-$ with ROH molecules the primary reaction involved major or exclusive formation of $F^-(HOR)_x$ ($x \geq 1$) cluster ions with the value of x varying with $\Delta H^\circ_{acid}(ROH)$. For example, the fast reaction of $(CF_3)_2CH^-$ with $(CF_3)_2CHOH$ produced a large amount of the cluster ion $(FH)^-OCH(CF_3)_2$[2] along with the product of exothermic H^+ transfer $(CF_3)_2CHO^-$ (eq 1). The related reaction of $(CF_3)_2CH^-$ with $(CH_3)_3COH$ gave initially only the cluster ion $F^-(HOC(CH_3)_3)_2$ as the observed product in a slower reaction.

$$\underset{m/z\ 151}{(CF_3)_2CH^-} + HOCH(CF_3)_2 \rightarrow$$

$$\underset{m/z\ 187}{(FH)^-OCH(CF_3)_2} + CF_3CH{=}CF_2 \qquad (1a)$$

$$\rightarrow \underset{m/z\ 167}{(CF_3)_2CHO^-} + (CF_3)_2CH_2 \qquad (1b)$$

Studies of gas-phase base (B^-) induced elimination reactions of fluoroethanes,[5] fluoroethenes,[6] and certain β-fluoro alcohols[7,8] usually involve formation of free F^- and FHB^- cluster ions, conjugate bases of the neutral reactants, and other product anions depending on the base and neutral reactant used. A simplified mechanistic assumption for the reactions of the fluoroethanes with B^- would be that F^- would result from an anti-E2 elimination while the cluster ions FHB^- were formed by a syn-E2 or E1cb mechanism.[9] The collision complex (fluoroethyl anion/HB) would be an intermediate in the E1cb process (eq 2).



(2)

The structures of negative ions formed by deprotonating partially fluorinated alkanes and alkenes other than those of the corresponding carbanions have been approached theoretically. Bach et al.[10] showed that the 4-31G geometry optimization of

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(1) McDonald, R. N.; Chowdhury, A. K.; McGhee, W. D. *J. Am. Chem. Soc.* **1984**, *106*, 4112–4116. $\Delta H_f^\circ((CF_3)_2CH^-) = -330.1 \pm 2$ kcal mol^{-1}.

(2) For cluster ions produced where $\Delta H^\circ_{acid}(HF) < \Delta H^\circ_{acid}(ROH)$, the low energy structure will be $(FH)^-OR$, while for the cluster ions where $\Delta H^\circ_{acid}(HF) > \Delta H^\circ_{acid}(ROH)$ the low energy structure is $F^-(HOR)$;[3] $\Delta H^\circ_{acid}(HF) = 371.5 \pm 2$ kcal mol^{-1}.[4a]

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