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THERMOCHEMICAL FEATURES OF SOME β-DIKETONES AND THEIR FRAGMENTS IN THE GAS PHASE

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UDC 541.11:547.442-13

The enthalpy of formation (EF) of cations and radicals in the gas phase is the key value in calculations of reaction enthalpies and predictions of the direction for molecular fragmentation by the action of electron impact. In a continuation of our work on the determination of the EF of cations and radicals [1] using data on the ionization potentials (IP) of molecules and the appearance potentials (AP) of ions obtained by photoionization, we treated diketones, the thermochemical characteristics of the fragments of which had not been studied. As in our previous work [1], we selected a series of $PhCOCH_2COR$ compounds (Table 1) with the common fragment $PhC(OH){=}CHC{\equiv}O^+$, the formation enthalpy of which is 562.8 kJ/mole; this value was found by calculation using the following equation:

$$\text{ПП}(A^+) = \Delta H_f{}^0(A^+) + \Delta H_f{}^0(B) - \Delta H_f{}^0(AB).$$

This value was used to find the EF of the radicals for which EF values were unknown ($C_3F_7{}^\bullet$ and $C_6F_{13}{}^\bullet$) or required refinement ($\Delta H_f{}^\circ$ cyclo-$C_6H_{11}{}^\bullet$ = 158.2 kJ/mole [2]).

The EF for $R'C(OH){=}CH{\equiv}O^+$ ions (R' = Ph, Me, 2-C_4H_4O, Me_3C and CF_3) permitted us to evaluate the contribution of these groups to the stabilization of this ion by comparison of the "reaction energies" Q of formal isodesmic reactions of the type

$$\begin{array}{ccccccc} MeC(OH){=}CHC{\equiv}O^+ & + & PhC(OH){=}CHCOMe & \rightarrow & PhC(OH){=}CHC{\equiv}O^+ & + & MeC(OH){=}CHCOMe \\ \Delta H_f{}^0 = 440.7 \text{ kJ/mole} & & -251.3 & & 562.8 & & -384.4 \end{array}$$

The value of the reaction heat Q indicates that the replacement of a methyl group by a phenyl group stabilizes the cation by 11 kJ/mole. The analogous calculation for the stabilization energies of $R'C(OH){=}CHC{\equiv}O^+$ ions in comparison with $MeC(OH){=}CHC{\equiv}O^+$ gives values of 8.70 kJ/mole for $R' = C_4H_4O$, 26.40 kJ/mole for Me_3C and −57.91 kJ/mole for CF_3 (destabilization).

In examining the mechanism for the formation of $R'C(OH){=}CHC{\equiv}O^+$ ions, we assumed that the formation of that form which leads to the $R'C(OH){=}CHC{\equiv}O^+$ ion occurs without regard to the dependence on the contribution of each of the two possible enolic forms in the starting molecule in the molecular ion prior to its decomposition. In order to check this hypothesis, we studied two isomers: $CF_3C(OMe){=}CHCOMe$ (I) with $\Delta H_f{}^\circ(M)$ = −947.6 kJ/mole, IP 9.67 eV, AP$[M - CH_3]^+$ = 9.71 eV, AP$[M - CF_3]^+$ = 9.71 eV and $CF_3COCH{=}C(OMe)Me$ (II) with $\Delta H_f{}^\circ(M)$ = −947.6 kJ/mole, IP = 9.50 eV, AP$[M - CH_3]^+$ = 9.76 eV, AP$[M - CH_3]^+$ = 9.66 eV. The similarity of the thermochemical indices of these two isomers leads to similar values of $\Delta H_f{}^\circ[M - CH_3]^+$ = −154.2 and −149.3 kJ/mole for (I) and (II) and $\Delta H_f{}^\circ[M - CF_3]^+$ = 428.1 and 423.3 kJ/mole for (I) and (II), respectively. If we start from the structures of molecules (I) and (II), the $[M - CH_3]^+$ and $[M - CF_3]^+$ ions may have different structures, correspondingly, $CF_3C(OMe){=}CHC{\equiv}O^+$ and $CF_3COCH{=}C{=}O^+H$, and EF of which should differ significantly. For example, $\Delta H_f{}^\circ(MeC{\equiv}O^+)$ is 657.0 kJ/mole [3] which is 154.8 kJ/mole less than for the $H_2C{=}C{=}\overset{+}{O}H$ isomers [4]. However, the low AP for the $[M - CH_3]^+$ and $[M - CF_3]^+$ ions and the comparison of the EF of these species with those those for their homologs $CF_3(OH){=}CHC{\equiv}O^+$ (Q = 52.7 kJ/mole) and $MeC(OH){=}CHC{\equiv}O^+$ (Q = 36.3 kJ/mole) indicate the identical nature of their structures from isomers (I) and (II). This implies that at 1,5-methyl shift may readily occur in their molecular ions prior to fragmentation,

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0568-5230/85/3407-1521$09.50

TABLE 1

Compound	ΔH_f° (M), enol, kJ/mole	IP (M), eV	AP $[M-R]^+$		ΔH_f° ($R^\cdot$)	ΔH_f° $[M-R]^+$
			eV	kJ/mole	kJ/mole	
$PhCOCH_2COR$						
R=Me	−251,3	9,10	9,90	955,2	143,5	560,4
Et	−273,0	8,90	9,77	942,6	107,5	562,1
CH_2Ph	−135,0	8,48	9,23	890,6	194,6	561,1
$CHPh_2$	−30,21	8,51	8,78	847,2	248,2	568,9
CF_3	−875,2	9,09	10,34	997,7	−438,9	561,4
	ΔH_f° (av.) $PhC(OH)=CHC\equiv O^+$					562,8
cyclo-C_6H_{11}	−319,4	9,09	9,63	929,2	47,00	562,8
n-C_3F_7	−1683	9,06	10,02	966,8	−1279	562,8
n-C_6F_{13}	−2913	9,00	10,10	974,6	−2501	562,8
$MeCOCH_2COMe$	−384,4	9,05	10,05	969,7	143,5	441,8
$MeCOCH_2COC_3F_7$	−1811	9,58	10,07	971,7	−1279	439,6
$Me_3COCH_2COCMe_3$	−528,4	8,94	9,57	923,4	43,93	351,0
$(2-C_4H_4O)COCH_2COCF_3$	−992,8	8,75	10,20	984,1	−438,9	430,2
CF_3COCH_2COMe	−1003	9,47	10,64	1026,6	143,5	−120,0

which justifies the above assumption of the possibility of a 1,5-shift of the more labile hydrogen atom in β-diketones.

EXPERIMENTAL

The enthalpies of formation of the β-diketones were taken or calculated from the data of Eastov et al. [5]. The Benson group contributions were used for these calculations [6]. The contribution of $[CF_3{-}C(OMe){=}] - [CF_3{-}(CO)] = -661.1$ kJ/mole was calculated from the data of Erastov et al. [5]. The values $[C-(F)_2(C)_{2F}] = -409.9$ and $[CF_3{-}C_F] = -676.5$ kJ/mole were taken from the work of Erastov [7]. In order to correlate the increments from the work of Benson [6] and Erastov [7], the contribution of $[C{-}(F_2)(CO)(C_F)]$ had to be changed from −402.3 [7] to −387.4 kJ/mole. From an analysis of the literature data for the contribution $[C_d{-}(C)(O)] = -189.5$ kJ/mole (Holmes [8] gave a value of −186.6 kJ/mole). The value for $\Delta\Delta H_f^\circ$ (ketone/enol) was taken in −10.0 kJ/mole [5]. The enthalpies of formation of the radicals were taken from Benson [6, 9]. $\Delta H_f^\circ(PhCH_2^\cdot) = 194.6$ kJ/mole (the mean value from several data [9]). $\Delta H_f^\circ(CH_3^\cdot)$ from our previous work [1] was recalculated for a new increment $[CF_3{-}CH_H] = -696.3$ kJ/mole [7]. The method for finding the IP of the molecules and AP of the ions was described in our previous work [1]. The reproducibility for the IP values was ±0.02 eV while that for the AP values was from ±0.02 to ±0.05 eV. The diketones were obtained by Claisen condensation in the presence of alkaline catalysts or by the hydration of α-acetylenic ketones according to Kucherov [10].

CONCLUSIONS

1. Photoionization was used to measure the appearance potentials of the ions of β-diketones, $R'COCH_2COR$, where R' = Ph, R = Me, Et, CH_2Ph, $CHPh_2$, cyclo-C_6H_{11}, CF_3, n-C_3F_7, n-C_6H_{13}; R' = Me, R = C_3F_7; R' = CF_3, R = Me; R' = R = CMe_3; R' = $(2{-}C_4H_4O)$, R = CF_3.

2. The enthalpies of formation of $R'C(OH){=}CHC{\equiv}O^+$ ions (R' = Ph, Me, $2-C_4H_4O$, CMe_3, CF_3) and of the cyclo-$C_6H_{11}^\cdot$, n-$C_3F_7^\cdot$, n-$C_6F_{13}^\cdot$ were determined.

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