photoproducts that have lost one or more CO ligands, such as $Mn(CO)_x$ ($x < 5$) and $Mn_2(CO)_y$ ($y < 9$).

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Heats of Formation and Homolytic Bond Dissociation Energies in the Keto–Enol Tautomers C_2H_4O, C_3H_6O

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The measurement of appearance energies (AE) for ionic fragments whose heats of formation (ΔH_f) are well-known can lead to accurate ΔH_f values for the *neutral* product of the dissociative ionization. Work in this laboratory has yielded ΔH_f for the enol forms of acetaldehyde and acetone[1] and a number of simple organic free radicals.[2] The *structure* of the neutral product of an ion fragmentation for which a metastable peak is observed can be assigned via its collision-induced dissociative ionization (CIDI) mass spectrum. The latter can be obtained by the use of a double-focusing mass spectrometer of reversed geometry (e.g., V.G. Analytical ZAB-2F) which has been slightly modified[3] to permit only neutral fragmentation products to enter the collision cell[4–6] situated in the second field free region of the instrument.

We report here measurements of ΔH_f for the radicals $\dot{C}H_2CHO$ and $\dot{C}H_2COCH_3$ and have derived the homolytic bond dissociation energies (HBDE) $D[H{-}CH_2CHO]$, $D[H{-}OCHCH_2]$, $D[H{-}CH_2COCH_3]$, and $D[H{-}OC(CH_3){=}CH_2]$. The latter measurement yields a ΔH_f value substantially different from that derived from gas-phase kinetic studies[7] and the associated HBDE is now in close agreement with the correlation between HBDE values and the barriers to internal rotation in the radicals described by Nonhebel and Walton.[8]

The compound $CH_3COOCHCH_2$ has m/z 43 as base peak in its normal mass spectrum. The reaction $[C_4H_6O_2]^{+\cdot} \rightarrow C_2H_3O^+ + C_2H_3O\cdot$ is accompanied by an intense, narrow Gaussian-type metastable peak. The fragment ions m/z 43 have the structure $[CH_3C^+O]$ as was shown by measuring their collisional activation mass spectrum and comparing it with that for acetyl ions.[9] Since the above metastable peak is the only one present in the ion kinetic energy spectrum of $[CH_3COOCHCH_2]^{+\cdot}$, the structure of the neutral $C_2H_3O\cdot$ species could be examined by its CIDI mass spectrum. Experimental details have been described elsewhere,[3] but in brief, the mass selected $[C_4H_6O_2]^{+\cdot}$ (m/z 86) ions fragment unimolecularly in the linear second field free region of the ZAB-2F spectrometer. All ions are deflected away and the high velocity (kV) neutral fragments pass into a cell containing a gas (He) where they are ionized by collision and subsequently fragment. Mass analysis of the ions is performed by the electric sector which is placed after the cell. it was observed that the CIDI mass spectrum of the $C_2H_3O\cdot$ radicals was very closely similar to the charge reversal mass spectrum of $^-CH_2CHO$ anions,[10] showing that the radicals generated at energies near the dissociation threshold for $[CH_3COOCHCH_2]^{+\cdot}$ were $\dot{C}H_2CHO$. Accordingly we have measured the AE m/z 43 using energy-selected electrons.[11] The result, AE = 10.04 ± 0.05 eV, combined with $\Delta H_f[CH_3C^+O]$ = 156 ± 1 kcal mol^{-1} [12] and $\Delta H_f[CH_3COOCHCH_2]$ = −75.3 ± 0.1 kcal mol^{-1} [13] gives $\Delta H_f[\dot{C}H_2CHO]$ = +0.2 ± 2 kcal mol^{-1}. This ΔH_f for the radical is in fair agreement with the 3 ± 2 kcal mol^{-1} derived from gas kinetics experiments by Rossi and Golden.[14] The HBDE from the present value is $D[H{-}CH_2CHO]$ = 92 ± 2 kcal mol^{-1}. The strength of this bond can be compared with $D[H{-}CH_2CHCH_2]$ (86 ± 1 kcal mol^{-1}).[7] An O–H bond strength can also be obtained. With $\Delta H_f[CH_2CHOH]$ = −30 kcal mol^{-1},[1] the value $D[H{-}OCHCH_2]$ in vinyl alcohol is 82 ± 2 kcal mol^{-1}, somewhat less than the corresponding bond strength in phenol, 86.5 ± 2 kcal mol^{-1}.[7]

Similar experiments were performed on the compounds $CH_3COOC(CH_3){=}CH_2$ and $CH_3COCH_2COCH_3$; AE m/z 43 was measured in each case and its structure confirmed to be $[CH_3C^+O]$; the CIDI mass spectra of the neutral fragments were the same as that of charge-reversed $^-CH_2COCH_3$ anions.[10] AE m/z 43 from $CH_3COOC(CH_3){=}CH_2$ (ΔH_f = −84.1 kcal/mol^{-1}, by additivity[15]) was 9.88 ± 0.05 eV and from $CH_3COCH_2COCH_3$ (ΔH_f = −90.8 kcal mol^{-1}, by additivity[15]) was 10.20 ± 0.05 eV, giving values for $\Delta H_f[\dot{C}H_2COCH_3]$ of −12.3 and −11.6 ± 1 kcal mol^{-1}, respectively. It should be noted that AE values give *upper* rather than *lower* limits for the heats of formation of reaction products; however, the narrow metastable peaks accompanying the above fragmentations attest to the lack of either a significant kinetic shift or reverse energy barrier and so the observed AE values will be close to the reaction's thermochemical threshold.[16] Note that the effect of CH_3 substitution in these radicals (−12 kcal mol^{-1}) is the same as the difference in heat of formation of an aldehyde and its corresponding methyl ketone.[13,15] The mean value for $\Delta H_f[\dot{C}H_2COCH_3]$, −12 ± 1.5 kcal mol^{-1}, is in poor agreement with the value of −5.7 ± 1.8 kcal mol^{-1} selected in the recent review by McMillen and Golden.[7] However, we suggest that the latter value may be too high. Two HBDE values can be calculated from the new result, namely: $D[H{-}CH_2COCH_3]$ = 92 ± 1.5 kcal mol^{-1} ($\Delta H_f[CH_3COCH_3]$ = −51.9 kcal mol^{-1} [13]) and 78 ± 2.5 kcal mol^{-1} for the O–H bond in the enol of acetone, for which ΔH_f = −38 ± 1 kcal mol^{-1}.[1]

Recently, Nonhebel and Walton[8] showed that a good linear relationship exists between the barriers to rotation in radicals $[R{-}\dot{C}H_2]$ and the HBDE $D[H{-}CH_2R]$. The magnitude of the barrier increases as the odd electron becomes more delocalized in the radical. The radical $\dot{C}H_2COCH_3$ was anomalous, not lying on the line when its heat of formation was taken to be −6 kcal mol^{-1}, i.e., $D[H{-}CH_2COCH_3]$ = 98 kcal mol^{-1}. We have replotted their line in Figure 1 using the present value for $\dot{C}H_2COCH_3$ and

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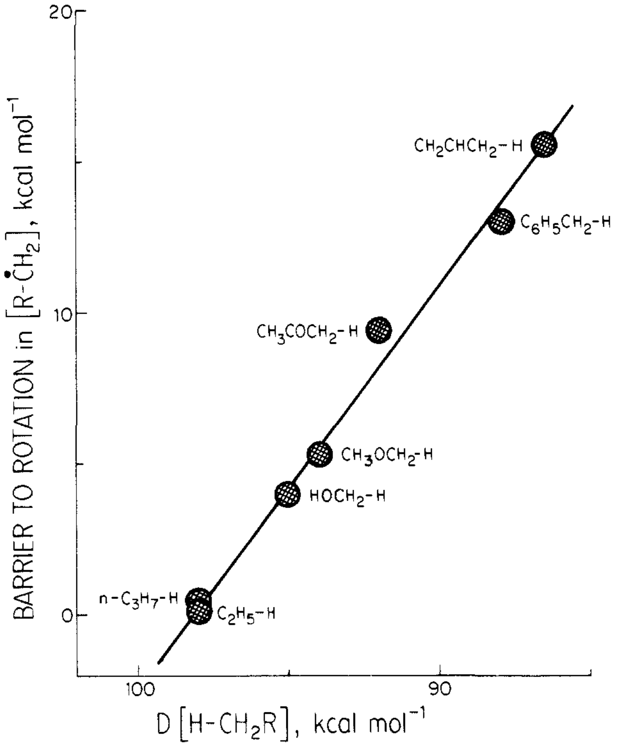

Figure 1. Plot of barrier to internal rotation in radicals [$R-\dot{C}H_2$] vs. homolytic bond dissociation energy $D[H-CH_2R]$. Points from ref 8 or as given in text.

two recent values of our own[2] for $\dot{C}H_2OCH_3$ and $\dot{C}H_2OH$.[3] The correlation is excellent and the new value removes the discrepancy for $\dot{C}H_2COCH_3$.

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Determination of the Interaction Free Energy Dispersion in Sorptive Systems by Relaxation Kinetics Methods

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We report here the direct measurement of sorption–desorption kinetics in a liquid chromatographic system. The sorption rate constants for an ion pair with homo- and heterogeneous octadecylsilicas have been determined by using the pressure-jump relaxation kinetics technique. The results indicate that the relaxation response curve is the Laplace transform of the distribution of first-order relaxations from the heterogeneous surface. Inversion of the relaxation curve permits determination of the mode in the sorption rate constant and a measure of the dispersion in interaction free energy of the solute with the surface.

For heterogeneous sorptive systems, there is a distribution of interaction energies. The particular width and form that this distribution takes may play an important if not critical role in determining the static and dynamic behavior of a sorptive system. For instance, it is known that the surface of chemically modified silica, as used as a stationary phase in HPLC, is heterogeneous with respect to surface silanol groups[1] and the local distribution of surface-bound molecules.[2,3] A heterogeneous surface may give rise to a phase where the kinetics of sorption–desorption are the dominant contributor to the overall chromatographic performance (bandwidth).[4] The kinetic contribution to band broadening may be as high as 70% or higher of the total elution bandwidth.[5] Chemical modification of silica yields a more energetically homogeneous surface.[6] This results in a reduction in peak dispersion and tailing in the chromatographic experiment, yielding a phase with higher "efficiency". Direct measurements of sorption–desorption kinetics in a chromatographic system show that differences in chromatographic efficiency are directly related to differences in sorption–desorption dynamics of test solutes on octadecylsilica stationary phases ("reversed-phase" HPLC).[7]

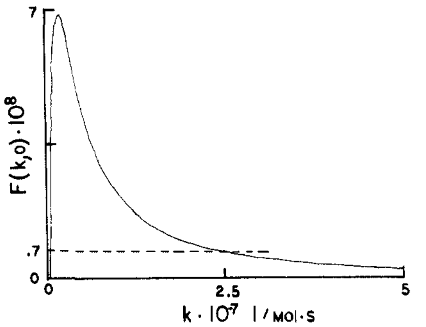

Figure 1. Function of eq 5 plotted for ODS-II, showing the dispersion (width at 10% of peak height) in the value of the desorption rate constant k_{-2}.

Two octadecylsilicas were synthesized for this study. Details of the synthetic procedure are reported elsewhere.[7] The two aliquots differ in levels of total carbon coverage, "ODS-I" containing 19.25% carbon and "ODS-II" containing only 12.25%. ODS-I is the more "efficient" of the two materials in terms of the elution peak width for test solutes when the materials are used as liquid chromatographic stationary phases.[7] From the considerations cited above, it is expected that ODS-I would be a more homogeneous material and thus show less dispersion in interaction free energy with solutes. The kinetic indicator for this pressure-jump relaxation experiment is an ion pair system in methanol at 25 ± 0.05 °C, involving a fluorescent sorption indicator, 1-anilino-8-naphthalenesulfonate, or "ANS", and high ("pseudoconstant") concentrations of trimethylhexadecylammonium counterion.[8] Details of the general experiment will be reported elsewhere.[7,9] The relaxation curve observed upon abruptly reducing the pressure from 2500 psi to atmospheric pressure has an initial fast step that is attributable to the primary sorption–desorption process, followed by a slow step that is due to pore intercalation effects.[7]

The relaxation kinetic data for the fast response for ODS-I are consistent with the following kinetic mechanism:

$$[A^-] + [C^+] \underset{k_{-1}}{\overset{k_1}{\leftrightarrow}} [A^-C^+] \tag{1}$$

$$[A^-C^+] + S \underset{k_{-2}}{\overset{k_2}{\leftrightarrow}} A^-CS^+ \tag{2}$$

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