

Energy Barriers for Exothermic Gas Phase Ion–Radical Recombinations

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The exothermic addition in the gas phase of a small radical to a heteroatom attached to a formal carbonium ion centre involves an energy barrier whereas addition to the carbonium ion centre involves little or none.

The great majority of direct bond cleavage reactions of odd and even electron positive ions in the gas phase have appearance energies (a.e.) the same as or slightly greater than those calculated from the product and reactant enthalpies. They are, therefore, often used to derive ionic heats of formation. Higher a.e. values can arise from a kinetic shift¹ (*i.e.* the rate constant for the reaction increases slowly with increase in internal energy) or from there being an *energy barrier for the reverse reaction*. Significant kinetic shifts for direct bond cleavages have, for example, been observed in aromatic molecules (*e.g.* the phenyl halides²) and the excess of energy in these cases is essentially statistically partitioned among the products' degrees of freedom³ leading to narrow, simple Gaussian type metastable peaks.⁴ In contrast, broad, flat- or dish-topped metastable peaks (resulting from non-statistical partitioning of the excess of energy) are observed for fragmentations involving a significant energy barrier for their reverse reaction.⁴

The ionised carbenes $[\text{HCOH}]^{+\cdot}$,^{5,6} $[\text{HOCO}]^{+\cdot}$,⁶ $[\text{CH}_3\text{COH}]^{+\cdot}$,⁷ and $[\text{HCNH}_2]^{+\cdot}$ ⁸ have recently been characterised as stable gas phase isomers of ionised formaldehyde, formic acid, acetaldehyde, and formalimine, respectively. The carbenes' heats of formation, ΔH_f° , have been measured^{6–8} and they are generally slightly greater than the ΔH_f° values for their conventional isomers, $[\text{H}_2\text{CO}]^{+\cdot}$, $[\text{HCOOH}]^{+\cdot}$, $[\text{CH}_3\text{CHO}]^{+\cdot}$, and $[\text{H}_2\text{CNH}]^{+\cdot}$. The above eight radical cations undergo a common fragmentation in the μs (metastable) time-frame, namely loss of $\text{H}\cdot$. The metastable peaks for the conventional ions' fragmentation are of simple Gaussian type. The kinetic energy releases, $T_{0.5}$ (measured from the peak width at half-height) are 170, 11, 43, and 65 meV respectively for ionised formaldehyde,⁶ formic acid,⁶ acetaldehyde,⁹ and formalimine⁸ and these four dissociations proceed at or close to the thermochemical threshold^{10–12} to yield $[\text{HCO}]^+$, $[\text{COOH}]^+$, $[\text{CH}_3\text{CO}]^+$, and $[\text{HCNH}]^+$. Thus the reverse reactions, addition of $\text{H}\cdot$ to a formal carbonium ion centre, have no appreciable energy barrier. In marked

contrast, the loss of the *hydroxy* or *amino* hydrogen atom^{6–8} from the carbenes generates dished or flat-topped metastable peaks and involves much larger kinetic releases, namely $T_{0.5}$ values of 370, 63 (Gaussian shape), 600, and 285 meV respectively. Furthermore, appearance energies of the above metastable peaks, measured by a comparative method,¹³ showed that the large kinetic energy releases indeed arose from the presence of a significant energy barrier. Each of these reverse reactions involves the addition of $\text{H}\cdot$ to the heteroatom adjacent to the carbonium ion centre.

In Table 1 are presented the enthalpy change and energy barrier (obtained from similar a.e. measurements) for nine reactions in which a radical is added to the heteroatom adjacent to a formal carbonium centre. Although the energy barriers for the last two reactions in Table 1 cannot be measured (because the reactions $[\text{CH}_2\text{XH}]^{+\cdot} \rightarrow [\text{CH}_3\text{X}]^{+\cdot}$, $\text{X} = \text{OH}, \text{F}$, take place below the dissociation threshold¹⁴) they have been evaluated by high level *ab initio* molecular orbital theory calculations (see Table 1). All the other energies have been shown to relate to the designated reactions. Note that for the corresponding reactions in which the radical is added to carbon, there is no energy barrier.¹⁰ Reaction (1) involves a significantly larger energy, 1.5 eV, than its isoelectronic analogue, (2).



It thus appears that attack of a small radical at the C atom requires little or no energy whereas reaction at the lone-pair possessing heteroatom has a substantial energy requirement.

This result, if indeed it is generally observed, will serve as a valuable guide for the prediction of mechanistic pathways both in ion–radical reactions and in unimolecular ion fragmentations. In particular the rule could be applied to reactions potentially occurring in the interstellar medium.

We propose that all these observations reflect the different electron densities at the attacked sites, with low electron density giving rise to a low energy barrier and vice-versa. For

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Table 1. Enthalpy change and energy barrier for ion-radical reactions (all values ± 0.1 eV).

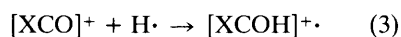
Reaction	Ref(s).	$\Delta H/\text{eV}$	Energy barrier/eV
$\text{H}\dot{\text{C}}\text{O} + \text{H}\cdot \rightarrow [\text{HCOH}]^{+\cdot}$	6	-0.4	1.1
$\text{CH}_3\dot{\text{C}}\text{O} + \text{H}\cdot \rightarrow [\text{CH}_3\text{COH}]^{+\cdot}$	7	0.0	1.35
$\text{HO}\dot{\text{C}}\text{O} + \text{H}\cdot \rightarrow [\text{HOCO}]^{+\cdot}$	6	-1.0	0.7
$\text{H}\dot{\text{C}}\text{NH} + \text{H}\cdot \rightarrow [\text{HCNH}_2]^{+\cdot}$	8	-0.9	1.5
$\dot{\text{C}}\text{H}_2\text{NH}_2 + \text{H}\cdot \rightarrow [\text{CH}_2\text{NH}_3]^{+\cdot}$	14	ca. 0	0.95
	15	-1.3 (calc.)	0.82 (calc.)
$\text{HO}\dot{\text{C}}\text{O} + \text{CH}_3\cdot \rightarrow [\text{HOCOCH}_3]^{+\cdot}$	7	-0.7	1.0
$\dot{\text{C}}\text{H}_2\text{OH} + \text{CH}_3\cdot \rightarrow [\text{CH}_2\text{O}(\text{H})\text{CH}_3]^{+\cdot}$	16	-0.4 (calc.)	1.4 ^a
$\dot{\text{C}}\text{H}_2\text{OH} + \text{H}\cdot \rightarrow [\text{CH}_2\text{OH}_2]^{+\cdot}$	14,17	-1.2	0.78 (calc.)
$\dot{\text{C}}\text{H}_2\text{F} + \text{H}\cdot \rightarrow [\text{CH}_2\text{FH}]^{+\cdot}$	14,18	-1.1	0.82 (calc.)

^a The m/z 46, $[\text{C}_2\text{H}_6\text{O}]^{+\cdot}$ ion was produced from ionised methoxyacetic acid (ref. 19); a.e. for metastable peak m/z 46 \rightarrow m/z 31 = 11.0 ± 0.1 eV. Calculated for $[\text{CH}_2\text{OH}]^{+\cdot} + \text{CH}_3\cdot = 9.6$ eV, from $\Delta H_f[\text{CH}_3\text{OCH}_2\text{COOH}] = -469$ kJ mol⁻¹ by additivity (ref. 20), $\Delta H_f[\text{CH}_2\text{OH}]^{+\cdot} = 707$ kJ mol⁻¹ (ref. 21), $\Delta H_f[\text{CH}_3\cdot] = 146$ kJ mol⁻¹ (ref. 22).

Table 2. Bond strengths in ion dissociations (± 0.1 eV).

Ion	$D[\text{C}-\text{R}]/\text{eV}$	Ref(s).	Ion	$D[\text{O}-\text{R}], [\text{N}-\text{H}], [\text{F}-\text{H}]/\text{eV}$	Ref(s).
$[\text{H}-\text{HCO}]^{+\cdot}$	0.95	10	$[\text{HCO}-\text{H}]^{+\cdot}$	1.5	6
$[\text{CH}_3\text{C}(-\text{H})\text{O}]^{+\cdot}$	0.5	10	$[\text{CH}_3\text{CO}-\text{H}]^{+\cdot}$	1.3	7
$[\text{H}-\text{COOH}]^{+\cdot}$	1.2	10	$[\text{HOCO}-\text{H}]^{+\cdot}$	1.7	6
$[\text{H}-\text{HCNH}]^{+\cdot}$	1.1	10	$[\text{HCNH}-\text{H}]^{+\cdot}$	2.4	8
$[\text{H}-\text{CH}_2\text{NH}_2]^{+\cdot}$	1.2	24	$[\text{CH}_2\text{NH}_2-\text{H}]^{+\cdot}$	0.95 (expt.)	14
				2.1 (calc.)	16
$[\text{H}_3\text{C}-\text{COOH}]^{+\cdot}$	1.4	11	$[\text{HOCO}-\text{CH}_3]^{+\cdot}$	1.7	7
$[\text{H}_3\text{C}-\text{CH}_2\text{OH}]^{+\cdot}$	0.85	10,11	$[\text{CH}_2\text{O}(\text{H})-\text{CH}_3]^{+\cdot}$	2.2	19
$[\text{H}-\text{CH}_2\text{OH}]^{+\cdot}$	0.8	14	$[\text{CH}_2\text{OH}-\text{H}]^{+\cdot}$	2.0	17
$[\text{H}-\text{CH}_2\text{F}]^{+\cdot}$	0.9	14	$[\text{CH}_2\text{F}-\text{H}]^{+\cdot}$	1.9	18

the reactions (3), where X = H, CH₃, OH, the magnitude of the energy barrier depends strongly on the nature of X, the substituent attached to the C atom, decreasing in the order CH₃ > H > OH. Note that this is not the order for carbonium ion stabilization, OH > CH₃ > H, but follows the relative electron affinities of X; for CH₃ 0.08 eV,²³ H 0.81 eV,¹⁰ and OH 1.83 eV.²³



From the measurements the O-R and N-H bond strengths can be calculated and compared with the corresponding C-R bond strengths; the former are much larger than the latter, as can be seen in Table 2. In the case of the only exception $[\text{NH}_3\text{CH}_2]^{+\cdot}$ there is a large discrepancy between theory and experiment which remains to be resolved.

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