Methyl Radical Expulsions Occurring with Kinetic Energy Release

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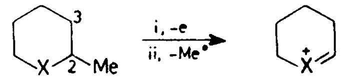
Summary Evidence is presented to show that a reaction channel exists for the addition of a methyl radical to the central carbon atom of a delocalised $-\ddot{X}-CH=\overset{+}{N}R-$ system (X = O or NH) requiring a kinetic energy of *ca.* 40 kJ mol^{-1}, since the delocalisation energy is lost in the addition process.

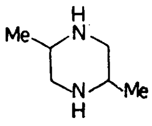
A USEFUL concept, which is supported experimentally, is that unimolecular dissociations into pairs of radicals or pairs of atoms, proceed such that the reverse process does not require a positive activation energy.[1] Similarly, in studies of the dissociation of gas-phase cation-radicals into cations and radicals, there is evidence to support the notion that the reverse processes normally involve a very small or negligible activation energy.[2] A notable exception is the loss of a methyl radical from a species derived by ionisation of benzyl methyl ether and some of its isomers; this dissociation occurs with release of kinetic energy (*ca.* 38 kJ mol^{-1}) in slow reactions occurring some 10^8 vibrations after excitation.[3] We now report a series of reactions in which methyl radicals are expelled with kinetic energy releases, and show that these processes are associated with a structural feature that results in the formation of extremely stable cations as the other products of dissociation.

The cation-radicals derived by ionisation of 2-methylpiperidine (**1**) and 2-methyltetrahydropyran (**2**) undergo methyl radical loss as their lowest activation energy unimolecular decompositions, and the metastable peaks accompanying these translations [(**1**) → (**3**) and (**2**) → (**4**)] are Gaussian and narrow, establishing the lack of a large kinetic energy release.[2] In contrast, if C-4 of the heterocyclic rings is replaced by a heteroatom (N or O), *e.g.* in (**5**)—(**7**), then the corresponding cation-radicals expel a methyl radical with a relatively large and specific release of kinetic energy (dish-topped metastable peaks). Relevant data are summarised in the Table.

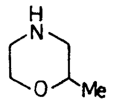


(**1**), X = NH
(**2**), X = O

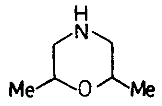
(**3**), X = NH
(**4**), X = O



(**5**)



(**6**)



(**7**)

Since the methyl radical is repelled from the transition state only in the presence of a second heteroatom, this heteroatom must be involved in the mechanism of the reaction. Clearly, in the cation-radicals which are initially produced, the C(2)–C(3) bond will be weakened towards homolysis [see (**8**)] as much as, or more than, the C(2)—Me bond, although C(2)–C(3) cleavage in (**1**) and (**2**) will have no consequences for methyl radical loss. However, in the case of (**5**)—(**7**), the product of C(2)–C(3) cleavage [*e.g.*, (**9**)] is ideally constituted for cyclisation *via* nucleophilic attack at C(2); a 1,2-hydrogen radical shift in

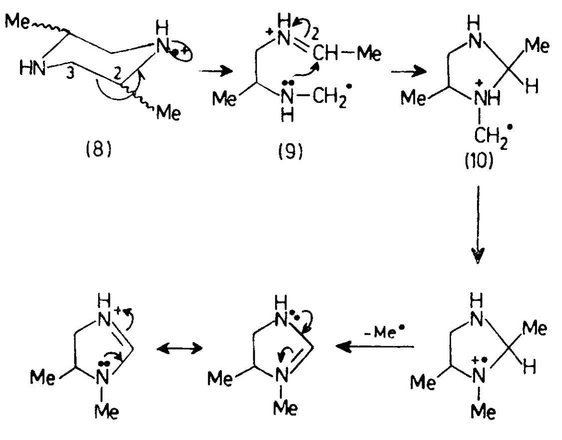
TABLE

Kinetic energy releases (*T*) in methyl radical expulsions

Compound	$m_1 \rightarrow m_2$	$w_{\frac{1}{2}}$/a.m.u.[a]	T/kJ mol^{-1}
(**5**)	114 → 99	0·91	36
(**6**)	101 → 86	0·87	41
(**7**)	115 → 100	0·91	36
(**11**)	114 → 99	0·91	36

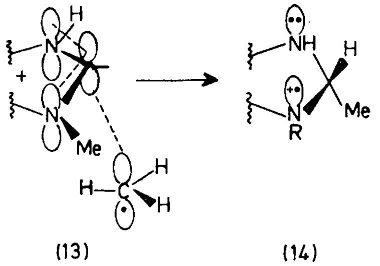
[a] Width of metastable peak at half-height (2nd field-free region, AEI MS9 mass spectrometer) (1 a.m.u. = 1 Dalton).

the product (**10**) can then produce ionised 1,2,5-trimethylimidazolide (**11**) from (**5**).



(8) (9) (10) (12) (11)

2-Alkylimidazolidines, like the corresponding oxygen heterocycles (ethylene acetals),[4] generally show no molecular ions, or very low abundance molecular ions in their mass spectra.[5] Thus, the most favoured unimolecular dissociations of these cation-radicals [*i.e.*, loss of the C(2) alkyl radicals] require zero or near zero activation energies. Dissociations which have effectively zero activation energies must be either thermoneutral or exothermic, the latter situation being statistically more probable among a collection of reactions. Thus the product combination [(**12**) + Me] is anticipated to be lower in energy than (**11**), and the difference in energies must appear as internal and/or kinetic energy (mutual repulsion) of the products. Our experiments show a considerable amount to be released as kinetic energy (Table). Evidently, in the reverse reaction, it is necessary to push the methyl radical into the centre atom of the delocalised π-system (**13**) to attain the localised system (**14**).



(13) (14)

In order to rest our hypothesis, we synthesised the neutral molecule corresponding to (**11**); N^2-methylpropan-1,2-diamine was synthesised by the literature procedure,[6] and converted into neutral (**11**) by reaction with an equimolar quantity of acetaldehyde in dry ether solution in the presence of anhydrous magnesium sulphate.[5] The ion (**11**), produced by direct ionisation of the 2,3,5-trimethylimidazolidine, expels a methyl radical with precisely the same release of kinetic energy (Table) as is found for the corresponding reaction of (**8**) [ionized (**5**)].

We thank Dr. S. Hammerum for the communication of results prior to publication and the Eleanor Sophie Wood Foundation for a travel grant (to J.R.K.).

(*Received, 2nd June* 1976; *Com.* 628.)

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[1] See for example, S. W. Benson, 'Thermochemical Kinetics,' Wiley, New York, 1968; P. J. Robinson and K. A. Holbrook, 'Unimolecular Reactions,' Wiley–Interscience, London, 1972, p. 155.

[2] R. G. Cooks, J. H. Beynon, R. M. Capriole, and G. R. Lester, 'Metastable Ions,' Elsevier, Amsterdam, 1973, p. 106.

[3] R. G. Cooks, J. H. Beynon, M. Bertrand, and M. K. Hoffman, *Org. Mass Spectroscopy*, 1973, **7**, 1303.

[4] J. T. B. Marshall and D. H. Williams, *Tetrahedron*, 1967, **23**, 321.

[5] S. Hammerum, personal communication.

[6] M. Saburi, Y. Tsujito, and S. Yoshikawa, *Inorg. Chem.*, 1970, **9**, 1476.