

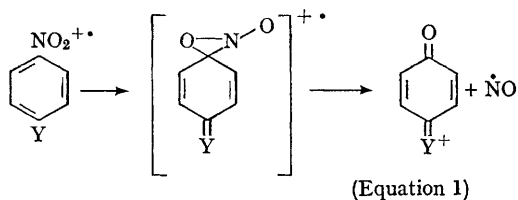
A Technique for Studying Structural Details of Gaseous Ions. Substituent Effects on "Flat-topped Metastable Ions" Associated with the Loss of CO from Molecular Ions of 2-Pyrones

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"FLAT-TOPPED metastable ions" are associated with the expulsion of small stable species in mass spectral decompositions with the production of excess kinetic energy.^{1,2} There is an apparent substituent effect on the amount of kinetic energy released in the loss of NO from molecular ions of substituted nitrobenzenes; certain electron-donating substituents—dimethylamino, amino, hydroxy, methoxy, and phenyl—in the *para*-position increase the energy released in a fashion related by resonance parameters.³ Presumably this variation reflects the ability of the substituent to stabilise the ionic product by resonance (see eq. 1).

On the other hand, if the structure of some product immediately formed by bond rupture is



such that the substituent cannot stabilise the ion by resonance, then there should be no appreciable

TABLE

Energy released in metastable decompositions of substituted pyrones†

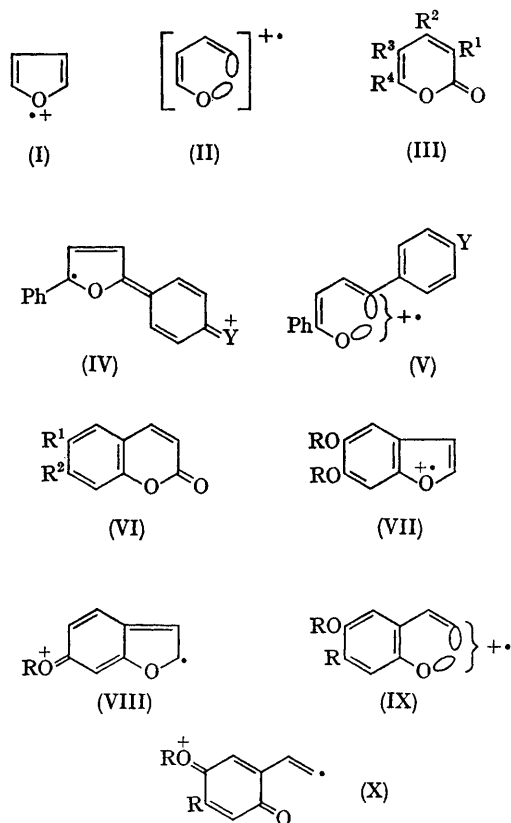
Compound	Substituents	Transition	<i>T</i> (ev)
(IIIa)	R ¹ = R ⁴ = Ph; R ² = R ³ = H	248 → 220	0.18 ± 0.04
(IIIb)	R ¹ = <i>p</i> -MeOC ₆ H ₄ ; R ⁴ = Ph; R ² = R ³ = H	278 → 250	0.16 ± 0.04
(IIIc)	R ¹ = <i>p</i> -PhC ₆ H ₄ ; R ⁴ = Ph; R ² = R ³ = H	324 → 296	0.15 ± 0.05
(IIId)	R ¹ = α -C ₁₀ H ₇ ; R ⁴ = Ph; R ² = R ³ = H	298 → 270	0.15 ± 0.05
(IIIe)	R ¹ = R ² = R ³ = H; R ⁴ = Ph	172 → 144	0.14 ± 0.04
(IIIf)	R ¹ = R ³ = H; R ² = R ⁴ = Ph	248 → 220	0.18 ± 0.04
(IIIg)	R ¹ = R ⁴ = H; R ² = R ³ = Ph	248 → 220	0.17 ± 0.04
(VIa)	R ¹ = R ² = H	146 → 118	0.17 ± 0.03
(VIb)	R ¹ = H; R ² = HO	162 → 134	0.20 ± 0.04
(VIc)	R ¹ = R ² = HO	178 → 150	0.18 ± 0.03
(VI d)	R ¹ = MeO; R ² = H	176 → 148	0.19 ± 0.04
(VIe)	R ¹ = H ₂ N; R ² = H	161 → 133	0.19 ± 0.04

† Recorded on a Hitachi RMU-6E mass spectrometer with direct insertion of the sample at 30° to 70°, except for (VIa) and (VI d) which were run *via* a heated inlet at 180°.

effect of the substituent on the amount of energy released. The loss of CO from substituted 2-pyrones is an example of this case. A description of the fragmentation of these compounds has been given,⁴ and further study with deuterium labelling was said to indicate that the ion formed by the loss of CO from the molecular ion of 2-pyrone is not symmetrical.⁵ Recently this interpretation has been questioned.⁶

The simplest representation of the C₄H₄O⁺ fragment formed by expulsion of CO from 2-pyrone is either (I) or (II), the choices corresponding to the symmetrical and unsymmetrical models respectively. If the parent compound is substituted so that a quinonoid intermediate is formed by the substituent, then substituent effects on the energy released in the formation of the intermediate could be compared with the effects of these substituents on the loss of NO from nitrobenzenes. Consider the compounds (IIIa), (IIIb), and (IIIc), the latter two have substituents which should be able to influence the resonance stabilisation of the product ion in (IV), but only after electronic reorganisation in (V), the alternate choice for the structure, where the orbitals left wholly or partially empty by the departure of CO are orthogonal to the π -system. No substituent effect outside experimental error is observed for the series (Table), in contrast to the effects found for the nitrobenzene series. There no release of kinetic energy is found in the parent compound, but *p*-nitroanisole and *p*-nitrobiphenyl ions decompose with release of 0.56 ± 0.06 and 0.38 ± 0.06 ev respectively.³

Consider now the coumarins (VI). In the case where a furan structure is supposed to result after loss of CO, we consider structures (VII) and (VIII); the product analogous to (II) is (IX). Again, resonance stabilisation in the latter case [indicated



by structures such as (X)] occurs only after electronic reorganisation. No significant increase in the amount of kinetic energy released occurs with substituents in either the 6- or the 7-position (Table). By comparison, the kinetic energy release

is 0.74 ± 0.06 eV in *p*-nitrophenyl and 0.85 ± 0.04 eV in *p*-nitroaniline.

None of the molecular ions of compounds (III d—g) decomposes with any significant change in the amount of kinetic energy released. Substitution by aromatic groups at various positions does not appear to afford new structural types easily attainable by the product ions.

We conclude that resonance stabilisation of $(M - CO)^+$ by substituents is not significant in substituted pyrones where certain structures might have suggested it by analogy. To this extent structures (IV), (VIII), and (X) are less appropriate representations than structures (V) and (IX). Many other structures could accommodate the data, which imply only a structure where the substituent is incapable of resonance with the charge. Similarly, the data support structure (II)

more than they do (I), but the adoption of a generic structure is of course a recognised extrapolation. Indeed, the use of the singular form of the noun "structure" is also an assumption.

The technique employed here may have some generality. Although the extent to which "flat-topped metastable ions" occur in mass spectra is not clear from a survey of the literature, in cases where they do appear, substituent effects on their width may be employed to divide them into two broad categories—"substituent-dependent metastables" and "substituent-independent metastables"—and these categories may be related to the stereoelectronic details of the product ion.

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