## Flash Photoionization Studies with Kinetic Mass Spectrometry

*Sir:*

We have recently succeeded in extending the technique of flash photolysis to the quantitative, time-resolved study of rapid gaseous ion–molecule reactions. We assembled an apparatus consisting of a high-intensity Garton-type vacuum uv flash lamp attached to a fast-response quadrupole mass spectrometer and a fast-flow reaction system, which made it possible to follow the intensity variation with time of a preselected photoion. The photoionization region was determined by the short-wavelength cutoff of the LiF window employed at 1050 Å and the appearance potential of the absorbing material.

Several systems have been investigated. Illustrative examples of ion intensity–time profiles are displayed in Figure 1 and a set of rate constants measured in comparison with those earlier reported in the literature is given in Table I.

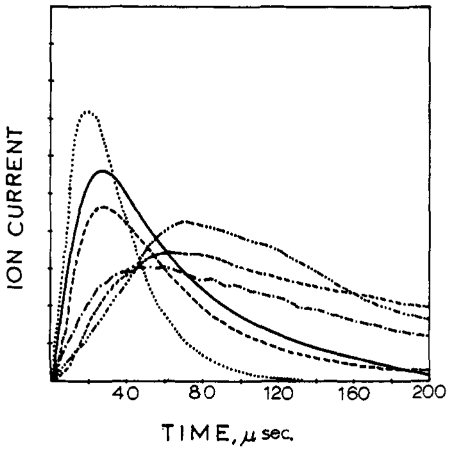

Figure 1. Illustrative examples of ion intensity–reaction time profiles (ion current in arbitrary units): ——, $NO^+$; -·-·-·, $(NO)_2^+$; ......, $C_4H_8^+$ from ethylene reaction; – – –, $C_6H_{12}^+$ from propylene reaction; –·······, $C_9H_{18}^+$ from propylene reaction; ·––––·–––, $C_6H_{12}^+$ from cyclopropane reaction.

The data show some scatter and the reproducibility of single measurements is within a factor of 2.5, which, in the case of five readings, as with cyclopropane, decreases to a value of less than two. Within these limitations the total rate constants for a given ion do not exceed the value given by the Gioumousis–Stevenson formula, and are independent of pressure. Also from a pressure study of cyclopropane the ratio of condensation to disproportionation, $k_{(10)}/\Sigma k_{(11-17)}$ shows an increasing trend with increasing pressure, as expected. Thus, while there is ample room for further improvement in accuracy, the present technique for ion–molecule rate constant measurements offers the following advantages. (a) The only primary ion formed is the parent molecule ion with little or no excess energy. (b) The reaction, or more precisely the reactant and product ion relative intensities, are displayed continuously on an absolute time scale, and consequently evaluation of the data does not require special kinetic assumptions. (c) The ions are drawn from the ionization chamber by flow rather than by

**Table I.** Absolute Rate Constants for Some Ion–Molecule Reactions[a]

| Reaction | Present[b] | Lit. | Ref |
|---|---|---|---|
| 1. $C_2H_4^+ + C_2H_4 \rightarrow C_3H_5^+ + CH_3$ | 3.3 | 7.3[d] | *h* |
| 2. $C_2H_4^+ + C_2H_4 \rightarrow C_4H_7^+ + H$ | 1.5 | 0.63 | *h* |
| 3. $C_2H_4^+ + C_2H_4 \rightarrow C_4H_8^+$ | 2.5 | 0.065[e] | *i* |
| 4. $C_3H_6^+ + C_3H_6 \rightarrow C_3H_7^+ + C_3H_5$ | 0.61 | 2.7 | *j* |
| 5. $C_3H_6^+ + C_3H_6 \rightarrow C_4H_7^+ + C_2H_5$ | 0.46 | 2.0 | *j* |
| 6. $C_3H_6^+ + C_3H_6 \rightarrow C_4H_8^+ + C_2H_4$ | 1.1 | 3.3 | *j* |
| 7. $C_3H_6^+ + C_3H_6 \rightarrow C_5H_9^+ + CH_3$ | 0.22 | 2.2 | *j* |
| 8. $C_3H_6^+ + C_3H_6 \rightarrow C_6H_{12}^+$ | 5.5 | | |
| 9. $C_6H_{12}^+ + C_3H_6 \rightarrow C_9H_{18}^+$ | 1.3 | | |
| $NO^+ + 2NO \rightarrow (NO)_2^+ + NO$ | 33[o,p] | 5 | *g* |

| Reaction | Present[c] | Lit. | Ref[n] |
|---|---|---|---|
| 10. $c\text{-}C_3H_6^+ + c\text{-}C_3H_6 \rightarrow C_6H_{12}^+$ | 0.33 ± 0.08[f] | | |
| 11. $c\text{-}C_3H_6^+ + c\text{-}C_3H_6 \rightarrow C_5H_9^+ + CH_3$ | 0.98 ± 0.27 | 0.095[d] | *m* |
| 12. $c\text{-}C_3H_6^+ + c\text{-}C_3H_6 \rightarrow C_4H_8^+ + C_2H_4$ | 5.4 ± 1.0 | 0.95 | *k* |
| 13. $c\text{-}C_3H_6^+ + c\text{-}C_3H_6 \rightarrow C_4H_7^+ + C_2H_5$ | 2.8 ± 0.4 | 0.33 | *l* |
| 14. $c\text{-}C_3H_6^+ + c\text{-}C_3H_6 \rightarrow C_3H_7^+ + C_3H_5$ | 0.41 ± 0.16 | 0.15 | *k* |
| 15. $c\text{-}C_3H_6^+ + c\text{-}C_3H_6 \rightarrow C_3H_5^+ + C_3H_7$ | 1.0 ± 0.17 | | |
| 16. $c\text{-}C_3H_6^+ + c\text{-}C_3H_6 \rightarrow C_3H_4^+ + C_3H_8$ | 0.27 ± 0.07 | | |
| 17. $c\text{-}C_3H_6^+ + c\text{-}C_3H_6 \rightarrow C_3H_3^+ + C_3H_8 + H$ | 0.56 ± 0.28 | | |
| $\Sigma k$ (11–17) | 11.4 | | |

[a] Rate constant × $10^{10}$ cc molecule$^{-1}$ sec$^{-1}$. [b] Pressure = 100 $\mu$. [c] Pressure = 140 $\mu$. [d] When reaction cross sections were given in the literature, rate constants were calculated from them using the equation given by Gioumousis and Stevenson [G. Gioumousis and D. P. Stevenson, *J. Chem. Phys.*, **29**, 294 (1958)]. [e] Calculated from a third-order rate constant for $p(C_2H_4) = 100\ \mu$. [f] The errors quoted are standard errors for a confidence level of 90%. The rate constant values were derived on the basis of the following scheme: $A^+ + M \rightarrow B^+ + M$, rate constant $k$; $d[B^+]/dt = k[A^+][M] - k_d[B^+]$; $k = (\ln [B^+] + k_dt + \text{constant})/[M]\int([A^+]/[B^+])dt \simeq (\ln [B^+] + \text{constant})/[M]\int([A^+]/[B^+])dt$. To correct for the error introduced by neglecting the term $k_dt$, where $k_d$ is the decay constant of $B^+$, $k$ was determined from the slope as $t \rightarrow 0$ of a $\ln [B^+]$ *vs.* $\int([A^+]/[B^+])dt$ plot. [g] W. C. Lineberger and L. J. Puckett, *Phys. Rev.*, **186**, 116 (1969). [h] J. J. Myher and A. G. Harrison, *Can. J. Chem.*, **46**, 101 (1968). [i] F. H. Field, *J. Amer. Chem. Soc.*, **83**, 1523 (1961). [j] A. M. Peers, *J. Phys. Chem.*, **73**, 4141 (1969). [k] L. W. Sieck and J. H. Futrell, *J. Chem. Phys.*, **45**, 560 (1966). [l] A. G. Harrison and J. M. S. Tait, *Can. J. Chem.*, **40**, 1986 (1962). [m] R. F. Pottie, A. J. Lorquet, and W. H. Hamill, *J. Amer. Chem. Soc.*, **84**, 529 (1962). [n] For a review of rate constant values, see J. H. Futrell and T. O. Tiernan in "Fundamental Processes in Radiation Chemistry," P. Ausloos, Ed., Interscience, New York, N. Y., 1968, Chapter 4. [o] Pressure range 400 $\mu$ to 2 Torr. [p] Rate constant × $10^{-30}$ cm$^6$ molecule$^{-2}$ sec$^{-1}$.

electrical forces and the complications caused by acceleration of ions as indicated by a recent study[1] are avoided.

Correlation of the present data with the earlier literature values are in the order which could be accounted for by the significant differences in experimental conditions. For example, the earlier value of $k_3$ was obtained at 200°, using 100-eV electron energies and a cell accelerating voltage of 5 eV; the deviation is in the right direction.

The six values, for reactions 8–10 and 15–17 are reported here for the first time.

Finally, it might be worth mentioning that the rise of the $NO^+$ and $c\text{-}C_3H_6^+$ parent ion concentration curves were considerably slower than those of other primary ions studied indicating that the superexcited states of these molecules are relatively long lived with a lifetime in the microsecond region.

A more detailed account will be forthcoming at a later date.

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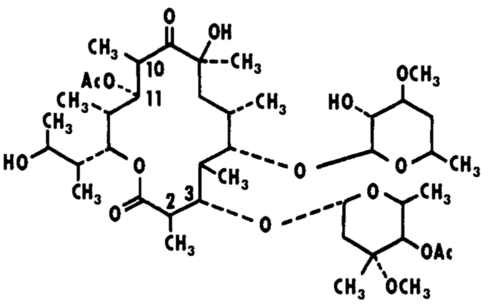
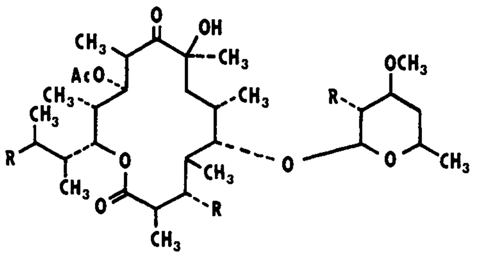
## Structure of Lankamycin

*Sir:*

Evidence obtained in these laboratories has shown that the structure of lankamycin is **1**, differing from the previously proposed structure[1] in that the sugar substitution is reversed; D-chalcose is bound at C-5 and 4-*O*-acetyl-L-arcanose is bound at C-3.



1



2, R = OH
3, R = OAc

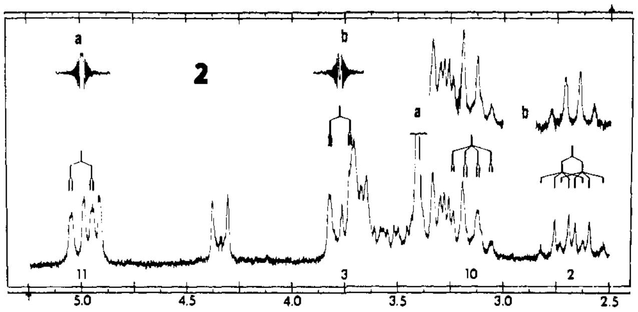


Figure 1. Partial nmr spectra of a $CDCl_3$ solution of darcanolide (**2**). Inserts show the decoupled spectra arising from irradiation at a and b, respectively.

Lankamycin, a neutral macrolide antibiotic[2] isolated from the fermentation broth of various *streptomycetes* species,[3,4] consists of a 14-membered polyhydroxylated lactone ring, 11-acetyllankolide,[1] on which are substituted two deoxy sugars, D-chalcose,[5] shown to be identical with D-lankavose,[5–7] and 4-*O*-acetyl-L-arcanose.[5,8] During mild methanolysis a monoglycoside, darcanolide (**2**), is formed together with methyl 4-*O*-acetyl-L-arcanoside.[1]

The partial nmr spectra of a $CDCl_3$ solution of **2**[9] (Figure 1)[10] reveals the resonances of two protons at 3.15 and 2.68 ppm ($\delta$) both coupled with a single additional ring proton and a methyl group. Detailed analysis of the nmr spectra of related macrolide antibiotics[11] and derivatives[12,13] has shown that the chemical shifts of these protons are indicative of protons $\alpha$ to a carbonyl group (*viz.* H-2 and H-10). Further, the conformation of the aglycone of **1** has been shown to be identical with that proposed for the aglycones of the erythromycins and related monoglycosides.[11–15] Therefore, the 3.15-ppm multiplet is assigned to H-10 on the basis of the small axial–equatorial $J_{10,11}$ coupling (1.5 Hz) and the 2.68 ppm resonance to H-2 by the large diaxial $J_{2,3}$ coupling (9.7 Hz).[16] These assignments were corroborated by spin decoupling experiments (Figure 1, a and b).[10]

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(9) Darcanolide was spectrophotometrically identical with a reference sample kindly provided by Dr. W. Keller-Schierlein, Eidg. Technische Hochschule, Zürich, Switzerland.

(10) Nmr spectra were determined at 100 MHz using a Varian Associates HA-100 spectrometer. Chemical shifts were obtained by first-order analysis and are reported in ppm ($\delta$) from internal reference TMS. Spin decoupling experiments were performed in frequency sweep using a Hewlett-Packard audiooscillator, Model 200AB.

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