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A NEW TECHNIQUE FOR STUDYING MECHANISMS OF MASS SPECTRAL REACTIONS USING C-14-LABELLED COMPOUNDS+

by

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For the investigation of reaction mechanisms and of the structure of rearrangement ions involved in electron impact induced reactions of organic molecules, well known advantages may be drawn from the use of specifically labelled molecules. To investigate changes of the carbon skeleton ^{13}C labelled substances have been used (1).

Stimulated by investigations of the electron impact induced fragmentation of terphenyls and higher polyphenyls in our laboratory (2), we have started another method to substitute specific carbon atoms using carbon-14. The essential feature of this method consists in producing, by means of a mass spectrometer with a focal plane, two different mass spectra of the ^{14}C labelled compound: a normal one, showing all mass lines, labelled and unlabelled, and a second one, obtained by autoradiography, showing only ^{14}C containing lines. No high resolution is required this way.

The method offers the following advantages compared to carbon-13 labelling:

1. ^{14}C labelled compounds are commercially available to a much larger degree and are less expensive than ^{13}C labelled ones.
2. The required mass spectral resolving power is only of the order of the mass number of the interesting molecules or fragments. Thus the method is especially suited for the investigation of molecules in the higher

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mass range, where resolution of the mass difference ($^{12}CH - {}^{13}C$) becomes difficult.

3. Small intensities of labelled ions can be detected in the presence of large amounts of unlabelled ions of the same nominal mass.
4. Double labelling with ^{14}C and ^{13}C may supply additional information using the method described here.
5. No difficulty with naturally occuring label content arises using ^{14}C.

EXPERIMENTAL

In order to check the method an inexpensive uniformly labelled benzene-C-14 has been used. A 33 mg amount of 1.7 mCi activity (4 mCi/mMol) was contained in a 300 cm^3 glass inlet system and entered into the Isatron type ion source of a CEC 21-110 Mattauch-Herzog type double focussing mass spectrometer through a suprasil leak.

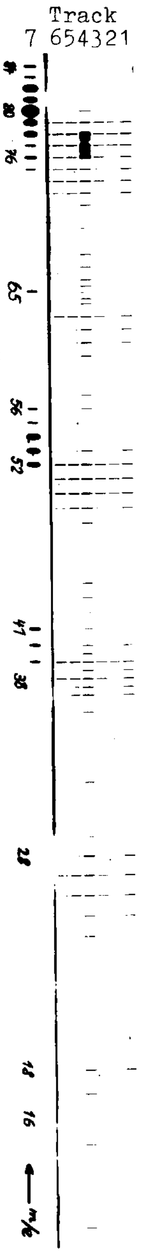
The mass spectrum was recorded first on an Ilford Q2 photographic plate, the position of the mass lines being fixed by simultaneously recording the ^{129}Xe peak at the Faraday collector of the combination detector.

In a second experiment the photographic plate was replaced by a graphite plate of same size manufactured from graphite EK 50 (Ringsdorff-Werke, West Germany) with smoothed surface. This plate was exposed during two days for a total of 16 hours. During this time a charge (ions + secondary electrons) of 5 x 10^{-4} coul was collected at the beam monitor between electric and magnetic sector fields, corresponding to an ionic charge of $\sim 10^{-4}$ coul collected at the graphite plate. About 1,4 mCi activity was consumed. All experimental parameters (pressure, ionizing current, potentials, resolving power) had been adjusted in order to obtain maximum ion current. The pressure in the ionization chamber could not be measured directly but is estimated to have been between about 5 x 10^{-4} and 5 x 10^{-5} Torr. The ionizing electron anode current was adjusted between 300 and 500 μA.

Throughout the experiment the ^{129}Xe peak was monitored at the Faraday collector. Small changes of the ion source potentials, which affected position or intensity of the ion beam thus could be observed and corrected. The experiment was run at the minimum resolving power of $M/\Delta M \simeq 500$, at which, from a previous experiment, the stability of the magnetic field was known to be sufficient not to shift the ^{129}Xe ion beam from the mass spectrometer exit slit over a period of several days. After exposure of the graphite plate a series of autoradiographs were taken from it on Kodirex-X-ray film (Kodak) and on Ilford Q2 plates. A small line producing β (^{14}C)-source was built in order to place calibration lines on each autoradiograph.

RESULTS AND DISCUSSION

The figure shows photographic reproductions of the total mass spectrum of benzene-C-14 at different exposures (track 1-6) and , in track 7, an autoradiograph of 168 hrs on Q2 plates. No difficulty arises when correalating both spectra and identifying ^{14}C containing lines.



Autoradiographs up to 335 hrs have been taken on Ilford Q2 plates and up to 90 hrs on Kodirex film. On the latter film lines became visible, the activity of which is about 10^{-4} times that of the most intense line at mass 80. Simultaneously a weak darkening appeared, which apparently was due to background radiation from the graphite plate. It covered only a stripe on the film containing the spectrum lines and not protected by a paper mask placed between plate and film. The background radiation was not observed in an autoradiograph of an unexposed plate and hence is supposed to arise from active benzene soluted in the surface region of the graphite plate during the experiment. Reducing the background pressure to below 10^{-6} Torr thus should make possible even longer autoradiograph exposures. From the ionic charge, sampled at the graphite plate, the relative intensities of the different mass lines, and the line geometry it was estimated that $\sim 3 \times 10^5$ electrons/cm^2 are sufficient to produce a visible darkening on Kodirex film, whereas Ilford Q2 plates were less sensitive by a factor of 4. However, probably due to better development conditions, we obtained lower background darkening on Ilford plates compared to Kodirex film, which in addition has a tinted base. No loss of activity on the collector plate due to sputtering - especially at the most intense active line at mass 80 - could be observed, and hence should be below the error limit of intensity measurements of $\sim$15%. This limit may be reduced to 5 - 10 % by improving dark chamber processing.

The line at mass 82 could be shown to result from twofold labelled benzene rather than from partly hydrogenated one, simply by comparing the ratios of the mass 80 and 82 intensities in the conventional and the autoradiographic mass spectra, which differed by a factor of 2. In order to solve the same question by high resolution a resolving power of $M/\Delta M \simeq 6500$ would have been necessary compared to 500 actually employed.

The experiment described above shows, that it is possible to collect high enough amounts of ^{14}C labelled ions on a target in the focal plane of a mass spectrometer in order to receive an autoradiographic picture of the mass lines containing ^{14}C. The required amount of activity is shown to be of the order of 1.5 mCi, if a dynamic range of 10^4 is required. It reduces to ~15 μCi, if a range of 10^2 is sufficient. This amount may be further reduced by extending the autoradiograph exposure time and by increasing the ionization efficiency, e.g. by resampling the un-ionized molecules. A more detailed report will be published later.

ACKNOWLEDGEMENT

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LITERATURE

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