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THERMOGRAVIMETRIC STUDIES OF POLYMERIC REAGENTS:
A POLYMERIC o-BENZYNE PRECURSOR

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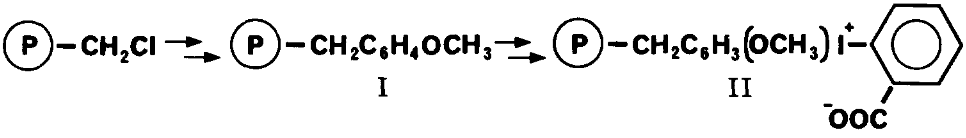
Abstract: Thermogravimetry for the study of polymeric reagents is described and used to demonstrate the thermic behavior of a polymeric o-benzyne precursor

Advantages of solid-phase synthesis are frequently offset by difficulties in polymer analysis. Recently, some authors applied thermal analysis to polymeric reagents[1], but only for studying their decomposition process under various conditions.

We are presently using the "Three-Phase Test", a method devised by us[2], to demonstrate aryne generation by fragmentation of polymeric o-substituted aryl compounds. In these studies, thermogravimetry permitted us to determine not only decomposition intervals, but degree of functionalization, reaction times, rate constants and other kinetic and thermodynamic parameters. The validity of the method was demonstrated for benzyne, as illustrated by the below experiments.

Polymeric benzyne precursor II[3] (eq. 1) was prepared from the Merrifield's resin by introducing methoxyphenyl groups[4], then treatment with o-iodosobenzoic acid:

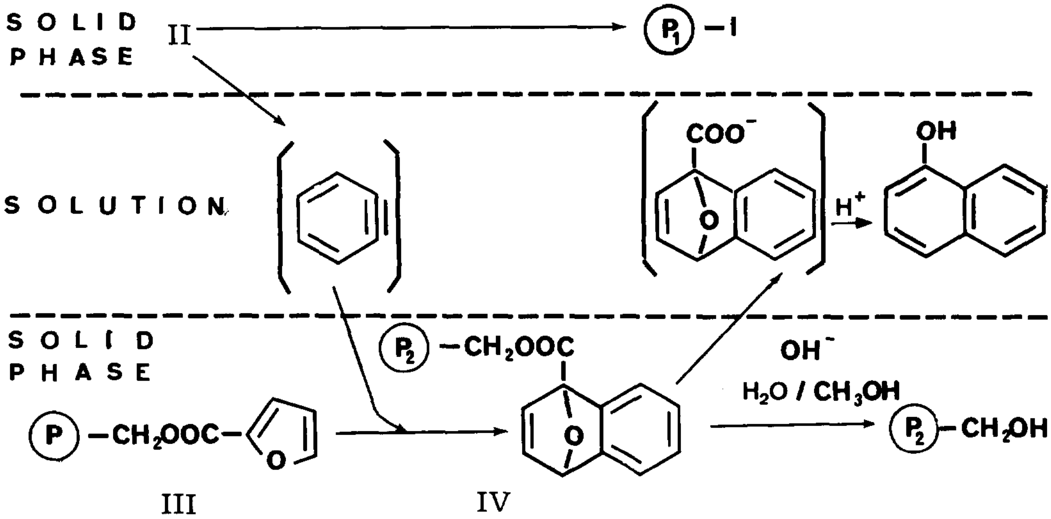


(1)

Application of three-phase test to II was accomplished by heating at 190º a suspension of II and trapping agent III[5](eq. 2) in triglyme/diethylbenzene, to yield polymeric adduct IV, from which α-naphthol was obtained by basic hydrolysis followed by acidification.

The isolation of naphthol supports the hypothesis that II generates

(2)



o-benzyne by thermic fragmentation. We then proceeded to study this fragmentation by thermogravimetry.

Figure 1 represents a non isothermal thermogravimetric analysis of II (a), chloromethylated resin (b) and methoxylated polymer I (c). We also analyzed a non polymeric compound analogous to II, diphenyliodonium-2-carboxylate (d):

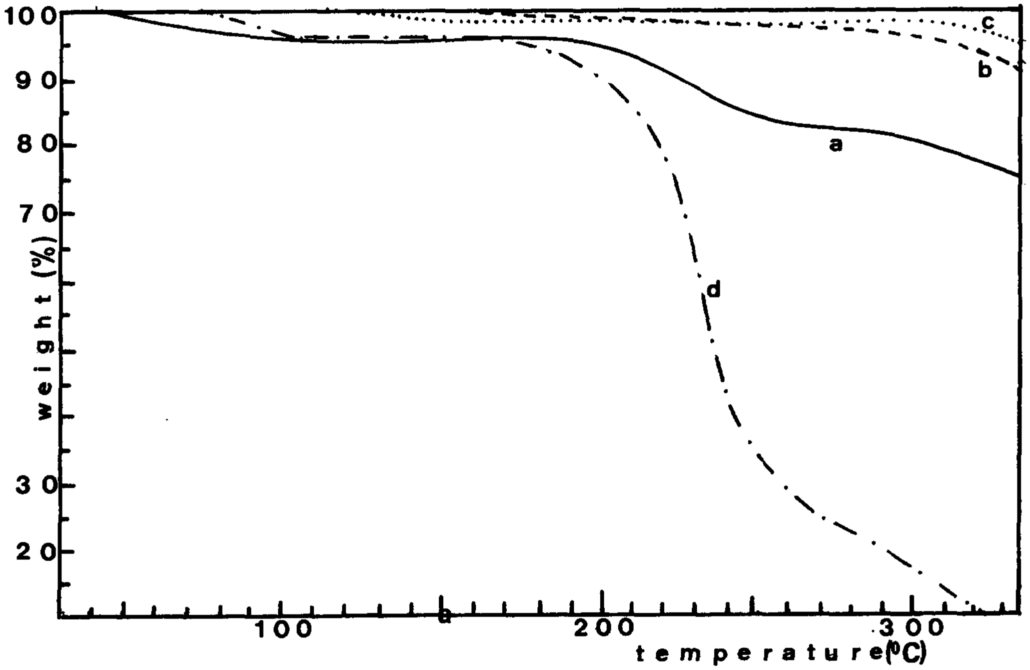
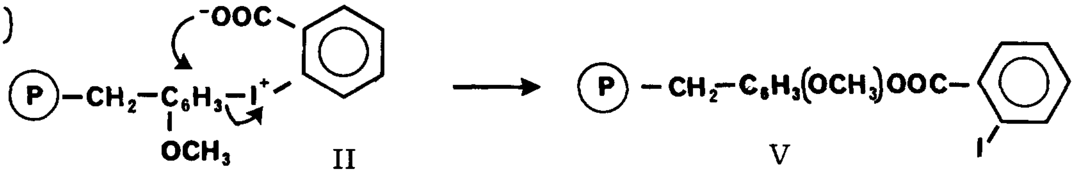


Fig. 1

While thermal reactions of I and Merrifield's resin (c & b) are similar, II (a) presents a loss in weight starting at 190º, due to benzyne generation. A similar reaction is shown by non polymeric diphenyl iodonium-2-carboxylate(d) Thermal loss is comparatively greater in this compound than in II, in which thermogravimetry indicates a yield of 1.25 meq diaryliodonium / g. resin.

IR analysis of polymer II after heating, suggest[6] that fragmentation and benzyne loss is accompanied by a rearrangement as indicated in eq. 3:

(3)



We can therefore assume that thermal treatment of II yields two reactions with two different rate constants:

$$\mathrm{II}\ \begin{matrix}\xrightarrow{k_1}\ \text{Benzyne (loss in weight)}\\ \xrightarrow{k_2}\ \text{V (no loss in weight)}\end{matrix}$$

From this we can deduce the kinetic equation:

$$- dm/dt = m_0 k_1 \exp(-(k_1 + k_2)t)$$

where m_0 is the initial mass of reactive phenyliodonium-2-carboxylate groups. A graph of $\ln(-dm/dt)$ in function of time should be linear, with a slope $-(k_1 + k_2)$ and intercept $\ln(m_0 k_1)$.

Isothermal thermogravimetry has permited us to perform such kinetic studies. Thermograms gave dm/dt against time and enabled us to determinate rate constants and thermodynamic activation data at each temperature, as shown in the Table:

Table

Kinetic and thermodynamic data in thermic reactions of II

T	$k_1 \times 10^4$	$k_2 \times 10^4$	Fragmentation process		
(ºK)	(s^{-1})	(s^{-1})	$\Delta H^{\ddagger}$ (cal/mol)	$\Delta G^{\ddagger}$ (cal/mol)	$\Delta S^{\ddagger}$ (cal/molºK)
478	22.6	2.8	31894	34454	- 5.36
488	43.2	13.7	31874	34507	- 5.40
498	91.8	44.7	31853	34562	- 5.44
508	158.1	55.9	31834	34616	- 5.88

From this table it can be assumed that the 1,4 fragmentation process in II is accompanied by a slower intramolecular process; k_2/k_1 ratio increases with the temperature, insinuating that it is better to accomplish thermic fragmentation of benzyne precursor at temperatures of about 200º, to avoid competitive reactions.

The activation energy for benzyne generation was established by ploting ln k_1 against 1/T, whose slope rendered 32850 cal/mol.

Therefore, thermogravimetry can orient us about polymeric reagents and reactions. Applications of this method to supposed precursors of arynes and hetarynes are in progress.

REFERENCES AND NOTES

1. Bothe, N.; Döscher, F.; Klein, J.; Widdecke, H., Polymer, 20, 850-854 (1979)
2. Rebek, J.; Gaviña, F., J. Am. Chem. Soc., 96, 7112-7114 (1974)
3. IR 1600, 1433, 1246, 1010 cm^{-1}
4. Polymer without methoxy groups is not likely to be a suitable substrate for Friedel-Crafts reaction with o-iodosobenzoic acid.
5. Gaviña, F.; Costero, A. M.; Gil, P.; Palazón, B.; Luis, S. V., J. Am. Chem. Soc., 103, 1797-1798 (1981)
6. Carboxylate band at 1600 cm^{-1} was substituted for a weaker one, at 1700 cm^{-1}

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