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Low-temperature Hydrobromination of Allyl Chloride and Autowave Regime of a Solid State Reaction

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Spontaneous hydrobromination of allyl chloride (AC) proceeds in the liquid phase (180–220 K, thermal effect $\Delta H = 17$ kcal mol^{-1}) to give 1-chloro-2-bromopropane; active centres produced by radiolysis at 77 K at the glass transition (87–95 K) initiate a chain addition reaction of HBr to AC to form 1-chloro-3-bromopropane (thermal effect $\Delta H = 13.2$ kcal mol^{-1}). This is the first example of hydrobromination at matrix devitrification; a local brittle fracture of the irradiated sample of AC + HBr gives an autowave of chemical conversion spread over the sample.

The photochemical hydrobromination of olefins at low temperatures has been described[1,2] and we have carried out investigations into radiational ethylene hydrobromination at 30–90 K.[3–5] This is the second example (after formaldehyde polymerization) of the phenomenon of low-temperature velocity limit to chain chemical reactions.[6]

A local brittle fracture in an extended sample of reactants produces a chemical reaction on the freshly-formed surface. Temperature or plane gradients arising in the reaction result in the further layer-by-layer dispersion of a solid sample. Due to this positive feedback an autowave of chemical conversion spreads over the sample. This autowave regime was observed for a wide spectrum of chain reactions at 4–77 K.[7,8] Because of considerable experimental difficulties an autowave of chemical conversion was not observed for the ethylene + HBr system and only critical conditions were studied,[3] hence it was interesting to study the autowave regime of hydrobromination in the allyl chloride (AC) + HBr system.

A liquid solution of the reactants ($\geqslant 180$ K) was quickly cooled to 77 K. Pure AC on cooling to 77 K passes to a glassy state. When such a sample is heated in a calorimeter[9,10] it turns from glass to an overcooled liquid ($T_g = 93$ K) that further crystallizes in the range 107–118 K and melts at $T_m = 136$ K (Fig. 1). An equimolar complex forms in the system $CH_2{=}CH_2 + HBr$.[11–13] Such a complex, with its own characteristic thermodynamic properties, has not been discovered for the AC + HBr system.

The spontaneous hydrobromination reaction in the system studied only takes place in the liquid state (see Fig. 1). The conversion in this temperature range is *ca.* 50%, and the degree of conversion is measured calorimetrically. Full conversion of HBr in a thermoactivated reaction occurs with an excess of AC. Thus, for HBr + AC (1:10), full conversion of HBr is observed, and the thermal effect is $\Delta H = 17 \pm 1$ kcal mol^{-1}.†

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† 1 cal = 4.184 J.

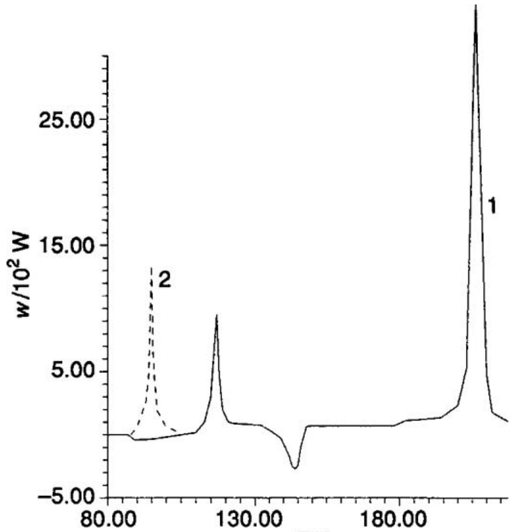

Fig. 1 Calorimetric heating curves for the HBr:AC = 1:1 system. 1, an unirradiated sample; 2, an irradiated sample, γ-pre-irradiation dose 1.5 kGy.

This value is in good agreement with the thermal effect of ethylene hydrobromination and the calculated value given in ref. 14.

Hydrobromination in the AC + HBr system may lead to formation of either 1-chloro-2-bromopropane or 1-chloro-3-bromopropane (by or against the Markovnikov law). The difference in the thermal effects of these two channels of addition consists in the difference of the C–H bond stability in methyl and methylene groups. In fact, the C–Br bond stability in 1-bromopropane and 2-bromopropane is the same, according to ref. 14 (*cf.* the stability of the C–H bond in propane in position 1, $\Delta H = 98$ kcal mol^{-1} and in position 2, $\Delta H = 94$ kcal mol^{-1}). Hence, the thermal effect of the addition reaction by the Markovnikov law is 4 kcal mol^{-1} higher than in the reaction against the law. Therefore, the experimentally measured thermal effect of spontaneous reaction of AC agrees with HBr addition by the Markovnikov law.

Radiolysis by ^{60}Co γ-rays at 77 K of the AC + HBr system leads to stabilization of active centres in the matrix which initiate an effective hydrobromination chain reaction on sample heating. This reaction takes place as the molecular mobility increases on heating in the system devitrification region (87–95 K) (Fig. 1). This is the first observation of chain hydrobromination at a glass transition. The conversion degree depends on the radiation dose and on the HBr concentration. Full conversion of HBr has already been observed for the HBr + AC system with ratios 1:20 and 1:60 and a pre-irradiation dose of 10 kGy. The thermal effect of such a post-radiation reaction measured for a series of experiments is $\Delta H = 13.2 \pm 0.5$ kcal mol^{-1}. Therefore, a post-radiation addition of HBr to AC leads to formation of 1-chloro-3-bromopropane (against the Markovnikov law).

A dose of more than 10 kGy activated the AC + HBr system so strongly that a spontaneous outburst of the reaction (at 77 K) could occur with any insignificant mechanical impact. In an unirradiated sample, a local mechanical fracture cannot start the hydrobromination reaction. Low-temperature radiolysis of the glassy equimolar AC + HBr system with a dose of 5 kGy leads to green colouring of a sample. A local brittle fracture of such a sample quickly forms a planar reaction front that propagates along the cylindrical sample axis with a constant velocity. When started from above, the autowave runs to the lower part of the cylindrical sample with a velocity of 0.016 ms^{-1}.

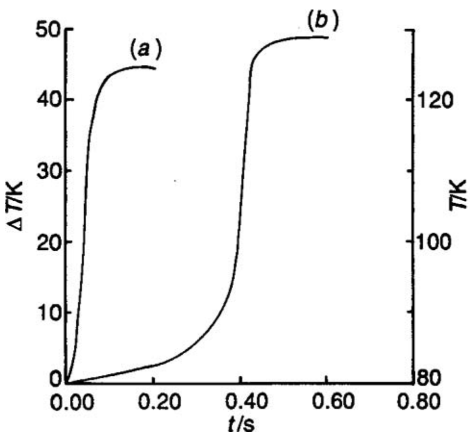

Fig. 2 A time sweep of a running temperature wave profile in an AC + HBr system previously irradiated by γ-rays of ^{60}Co at 5 kGy. (*a*) wave starting from the bottom of the sample, speed 0.16 ms^{-1}; (*b*) wave starting from the top of the sample, speed 0.016 ms^{-1}.

A characteristic temperature profile of a running reaction wave (change in time of a thermocouple signal frozen into the sample) is given in Fig. 2. The characteristic temperature profile (curve *b*) corresponds to a slow wave regime that was described for another reaction in detail in refs. 7 and 8. As the system heats in a narrow reaction zone within a short period of time, it is assumed to be adiabatic. Using the thermal effect of reaction, $\Delta H = 13.2 \pm 0.5$ kcal mol^{-1}, we may evaluate the HBr conversion degree as a result of the reaction wave running. As is seen from Fig. 2, curve *b*, the maximum heating of the system in the wave front is $\Delta T = 48$ K, and assuming a system heat capacity $c = 1.8$ kcal mol^{-1} K^{-1}, we derive for conversion depth $\Gamma = \Delta H / c\Delta T = 0.16$.

We demonstrated for the chain chlorination autowave that initiation of the reaction from the bottom of the sample increased the autowave velocity markedly.[15] When the hydrobromination autowave was started from the bottom of the sample in the AC + HBr system the running conversion wave parameters also appeared to be quite different. Fig. 2, curve *a*, gives a time sweep of a running temperature wave profile. As distinct from the wave starting from the top of the sample, steep temperature profiles are registered. The stage of pre-heating of a neighbouring layer is absent, and the velocity of wave propagation is increased ten times to 0.16 m s^{-1}. The maximum heating of the system in the running wave front in that case is $\Delta T = 43$ K, *i.e.* the degree of conversion HBr in the case of autowave initiation from the bottom of the sample is practically the same value as when initiated at the top, $\Gamma = 0.16$. As the conversion wave velocity in this case is ten times higher, the gross velocity of hydrobromination is increased by one order of magnitude.

References

1 G. B. Sergeev and A. P. Shvedchikov, *Zh. Vses. Khim. Ova im. D. I. Mendeleeva*, 1973, **18**, 52 (in Russian).
2 G. B. Sergeev and V. A. Batiuk, *Kriokhimiya* (*Cryochemistry*), M. Khimiya, 1978, p. 296 (in Russian).
3 D. P. Kiryukhin, I. M. Barkalov and V. I. Goldanskii, *Dokl. Akad. Nauk SSSR*, 1978, **238**, 388 (in Russian).
4 A. M. Zanin, D. P. Kiryukhin, I. M. Barkalov and V. I. Goldanskii, *Dokl. Akad. Nauk SSSR*, 1980, **253**, 142 (in Russian).
5 D. P. Kiryukhin, I. M. Barkalov and V. I. Goldanskii, *J. Chim. Phys.*, 1979, **76**, 1013.
6 V. I. Goldanskii, L. I. Trahtenberg and V. N. Flerov, *Tunnelnye Ayvleniay v Khimicheskoi Fizike* (*Tunnel Appearances in Chemical Physics*), Nauka, Moscow, 1986 (in Russian).
7 V. V. Barelko, I. M. Barkalov, V. I. Goldanskii, D. P. Kiryukhin and A. M. Zanin, *Adv. Chem. Phys.*, 1988, **74**, 339.
8 V. V. Barelko, I. M. Barkalov, V. I. Goldanskii, A. M. Zanin and D. P. Kiryukhin, *Usp. Khim.*, 1990, **59**, 353 (*Russ. Chem. Rev.*, 1990, **59**, 205).

9 I. M. Barkalov and D. P. Kiryukhin, *Vysokomol. Soedin, Ser. A*, 1980, **22**, 723 (in Russian).

10 I. M. Barkalov and D. P. Kiryukhin, *Khim. Vys. Energ.*, 1990, **24**, 387 [*High Energy Chem. (Engl. Transl.)*, 1990, **24**, 355].

11 A. M. Zanin, D. P. Kiriyukhin, I. M. Barkalov and V. I. Goldanskii, *Dokl. Akad. Nauk SSSR*, 1981, **260**, 1171 (in Russian).

12 G. N. Kovaliev and G. B. Sergeev, *Dokl. Akad. Nauk SSSR*, 1965, **160**, 390 (in Russian).

13 G. N. Kovaliev, *Vestn. MGU, Ser. Khim.*, 1976, **17**, 555 (in Russian).

14 J. D. Cox and G. Pilcher, *Thermochemistry of Organic and Organometallic Compounds*, Acad. Press, London, 1970.

15 D. P. Kiryukhin, P. S. Mozhaev and V. V. Barelko, *Khimicheskaya Fizika*, 1992, **11**, 264 (in Russian).

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