Reactions of Thermal Hydrogen Atoms with Propene at 77 K. Infrared Heating Effects in Solid Organics *in vacuo*

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Summary During a study, which showed that thermal hydrogen atoms generated on a tungsten filament do not in fact react rapidly with solid propene at 77 K, it was found that unexpectedly large i.r. heating effects may occur in refrigerated organic solids *in vacuo*.

Considerable work has been conducted on the reaction of gas-phase thermal hydrogen atoms with thin films (10^{-4} cm) of solid olefins at cryogenic temperatures. For propene in particular, it has been claimed without exception, that this reaction is rapid. Sustenance of such a rapid reaction has either been explained by free diffusion of hydrogen atoms into the solid[1,2] or by rapid turn-over of the olefin surface layers[3] or a combination of these models.[4] The atom diffusion model has not conformed well with kinetic results[3] while intrinsic rapid turn-over of the matrix at 77 K is an unacceptable scheme as it has been clearly shown in radiation chemistry that radicals formed in propene are firmly trapped at this temperature.[5]

The present communication concerns a portion of a lengthy study in which relatively thick films of propene (about 0·5 cm) were exposed to thermal hydrogen atoms generated in the standard fashion by pyrolysis of molecular hydrogen on a heated tungsten filament. Reaction rates were observed using the rate of fall of hydrogen pressure in a static system. The use of a two limbed reaction vessel shaped rather like an "H", allowed reactions to be studied in which the olefin was either positioned below the filament (the usual method) or in the limb remote from the filament. In this latter situation the reactant could be shielded from the light emitted by the filament when desired. The entire vessel was completely immersed in liquid nitrogen during the experiment.

Reactions conducted under the filament did indeed show rapid uptake of hydrogen although the rate for a glassy sample was 1·5 times faster than for a crystalline sample. However, for light-shielded samples not under the filament the glassy form reacted only slowly while for the crystalline sample reaction was not detectable even after more than twelve minutes. Conducting these latter type experiments in the light of an external tungsten lamp enhanced the uptake rate by the organic glass and initiated reaction with crystalline samples. That the effect of the light was the result of direct heating by the near i.r. (9·9—2·6 nm) was suggested by the observation of decreased reaction rates at higher hydrogen pressures as a result of enhanced heat transport to the walls. These conclusions are also supported by experiments in which the active wave lengths were removed by appropriate optical filters. Final confirmation of the hypothesis was obtained by making direct temperature measurements using two thermocouples embedded in the organic matrix in the remote limb. Both junctions were positioned centrally (diameter of vessel 2·6 cm), one at the gas–organic interface (T_1) and the other at the organic–Pyrex interface (T_2). Temperatures were measured under vacuum conditions and with 130 mTorr of helium. Temperatures recorded for these experiments are given in the Table.

The extent of the observed heating effect in the absence of any gas is surprisingly large. This can be explained by the fact that when an organic liquid is frozen it contracts away from the container walls producing a sample isolated from thermal contact with the walls such that normal conductivity processes cannot apply. Accordingly it was observed here that the matrix temperatures resulting from radiant heating depended intimately on the thermal conductivity of the gas present. Since the thermal conductivity of helium is better than that of hydrogen the reported temperatures are probably lower than those occurring during the normal hydrogen atom experiments. It is important to note that for propene in the remote limb the temperature at the gas–organic interface (upper surface) was actually above the melting point even with a pressure of 130 mTorr of helium. Thus the reaction of hydrogen atoms is with propene in the liquid state.

TABLE

Sample	Form	Temperature of matrix t/K[a] T_1	T_2	Helium pressure/mTorr
Propene	Crystal	91·5	85·7	130
m.p. 87·8 K		94·7	86·7	0
	Glass	89·2	84·2	130
		90·5	85·2	0
Isobutene	Crystal	96·2	93·2	130
m.p. 131·8 K		111·2	104·2	28
Allyl alcohol	Glass	116·2	106·2	130
m.p. 144 K		157·2	122·2	0

[a] The bath temperature is 77 K.

In the shielded experiments where heating is not significant, the inertness of solid propene to thermal hydrogen atoms can, despite the low intrinsic activation energy for the addition process,[6] be justified in terms of the extra energy required to reorient the bonds in order to accommodate the incoming atom in the solid phase. This reorientation requirement will be more restrictive for a molecule in a crystal lattice than for one in an amorphous glass but even in this latter case the reaction observed was not rapid. It is important to realize that if such reorientation is also inhibited for olefin molecules present at scavenger concentrations in other solid systems it is unlikely that these molecules can act as scavengers for thermal hydrogen atoms as is usually supposed.

A reassessment may be needed of results obtained in areas such as photochemistry, absorption spectroscopy, or e.s.r. spectroscopy involving photochemical activation, where temperature definition has depended on assuming rapid and sustained equalization between the temperature of a frozen organic substance and the walls of its container under vacuum conditions. The possible size of the temperature discrepancy in a given case would be expected to be smaller for samples with lower melting points and smaller dimensions. The dependence on melting points arises from the fact that when the organic layer at the Pyrex interface melts good thermal contact will be achieved and an oscillatory cycle of refreeze, melt etc., will begin at that interface which will limit the ultimate achievable temperature of the bulk of the organic. This conclusion is supported by the present results while with regard to sample size others have shown that even in a tube as small as 3 mm i.d. considerable heating can be observed.[7] In conclusion it should be pointed out that these heating effects can be avoided by adding helium or other heat conducting gas to the system prior to experimentation; a procedure which unfortunately has rarely been followed. It is clear that one cannot assume that an isolated organic matrix is actually at the temperature of the surrounding bath if the possibility of radiant heating exists.

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