# Some New Glass-Forming Hydrocarbon Mixtures

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In order to study in detail the photolysis reaction mechanisms in a high-viscosity matrix at 77°K it is necessary to devise conditions and means by which reaction between the photolytically active molecules and the surrounding matrix molecules can be prevented or elucidated. The hitherto used glasses [1-4] based on hydrocarbons consist of one or two of the compounds isopentane, 3-methyl pentane and methyl cyclohexane, all containing hydrogen attached to tertiary carbon atoms.

One of the predictable reactions between primary photolysis products and matrix molecules is the hydrogen abstraction from a hydrocarbon by a species of radical nature [5,6]. As the $C_{tert}$-H bond dissociation energy is about 5 kcal less than that for a $C_{sec.}$—H bond (89 and 94 kcal, respectively) [7], it should be advantageous to have available a matrix without tertiary carbon atoms in the hydrocarbon components. According to the Arrhenius equation, an increase in activation energy of 5 kcal at 77°K changes the rate constant by a factor of $10^{-14}$, provided the preexponential factor does not change. Hydrogen bonded to a tertiary carbon atom reacts instantaneously whereas hydrogen bonded to a secondary carbon atom does not react at all.

The following hydrocarbons were purified according to standard procedure [8]: pentane (a), isopentane (b), hexane (c), cyclohexane (d), 3-methyl pentane (e), *neo*-hexane (f), methyl cyclopentane (g) and methyl cyclohexane (h). Binary and ternary mixtures were made and repeatedly cycled between room temperature and 77°K to study their glass-forming properties. The tendency for cracking at 77°K was tested by filling sample tubes with small pieces of broken glass.

The following results were obtained. First, the components of the mixture are given and, secondly, the approximate volume ratio between them, for which a glass with given quality was obtained (in three cases a rather broad ratio interval is given for which glasses have been obtained).

Mixtures forming good glasses at 77°K: a:f, 3:5—3:10; b:e, 0:1—1:0.

Mixtures forming good glasses, which may crack when stored for hours at 77°K: a:c:f, 1:1:9; a:d:f, 5:2:13; b:e:h, 1:1:1; b:h, 3:2; d:f, 1:9; e:h, 1:2—1:6.

Mixtures crystallizing in all proportions during freezing: c:f, e:g, f:g, g:h.

Of the mixtures studied, a:f, a:c:f, a:d:f and d:f do not contain tertiary carbon atoms. However, the only one which has been found to give a very stable glass is pentane and *neo*-hexane. In the proportions 3:8, this glass has been extensively used in our laboratory.

Contraction between 298 and 77°K, relative viscosity and melting behaviour for some of these glasses have been studied [8].

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