

MECHANISMS OF DECOMPOSITION OF MIXTURES OF ETHYL ACETATE AND ISOPROPYL BROMIDE SUBJECTED TO PULSED INFRARED LASER IRRADIATION

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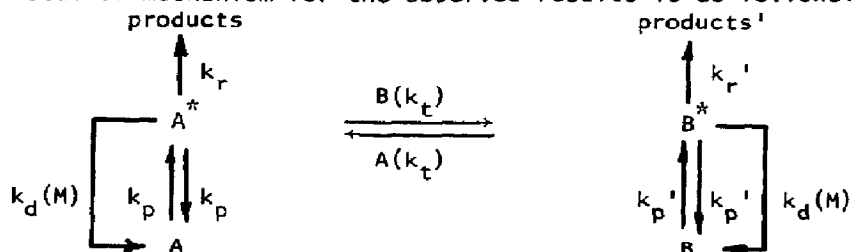
We are concerned with the decomposition of polyatomic molecules by multiphoton absorption of infrared radiation from a pulsed CO₂-TEA laser. This is a continuation of earlier work [1] using 3 to 1 mixtures of the absorbing ethyl acetate molecule and non-absorbing isopropyl bromide molecule over a pressure range of 0.5 to 50 torr. The mechanism of decomposition of both molecules is that for the lowest thermal dissociation channel [2],



The specificity of the decomposition processes at low pressure is demonstrated by product yields of ethylene that are far in excess of propylene assuming that these reactions proceed by a high pressure unimolecular equilibrium mechanism. We report here on studies with excess added inert gas (pressures up to one atmosphere), as well as with varying ratios of ethyl acetate and isopropyl bromide.

Figure 1 shows the effect of added He to the original 3 to 1 ethyl acetate/isopropyl bromide mixture. Figures 2 and 3 are similar, except that the ethyl acetate to isopropyl bromide ratios are being varied, the total change being a factor of 6. In all these figures the effect of adding helium is seen to be similar. There is a small decrease in specificity initially, but a relatively high level of specificity is maintained at pressures close to 1 atmosphere. The effect of reducing the ethylacetate/isopropyl bromide ratio is to increase reaction specificity across the whole range of pressures. Finally Figure 4 relates product yield to reactant pressure.

A detailed mechanism for the observed results is as follows:



This scheme provides an alternative mechanism for the apparent approach to thermal equilibrium at high total pressures (absence of helium) observed in this and earlier studies. That is, the decomposition of isopropyl bromide is not induced through simple heating. In the above sequence k's refer to pumping to and away from a low level bottleneck. The bottleneck is created by differences in the two pumping processes, k_p (produc-

tion of starred molecules) and k_r , (loss of starred species by pumping to higher dissociative channels). If, as is the case for ethyl acetate-isopropyl bromide mixtures, one molecule absorbs (molecule A) and the second (molecule B) does not, then $k_r' \approx 0$. The molecule B can get involved in the scheme only through collisional energy exchange. We introduce deactivative steps in the model in order to explain the effects observed when inert gas is added to the system.

This simple model is based on several assumptions. Some of these assumptions are subject to experimental verification. Because of the low lying bottleneck the system can never be entirely in thermal equilibrium except possibly at high total pressures. However, the lower manifold A^* and B^* can, at high pressures, be in equilibrium, while remaining in disequilibrium with the upper states. The above two step model assumes dissociation entirely by a photochemical mechanism. Any purely thermal component must be introduced in a different way. The time scale for reaction is therefore the time duration of the laser pulse. Introduction of large amounts of inert buffer gas assures of minimal thermal effects, or little post-laser chemistry. In order to assure that the dissociation rates for A and B approach the so called 'thermal' limit at high pressure, the rate parameters k_r and k_r' must be chosen in this thermal ratio.

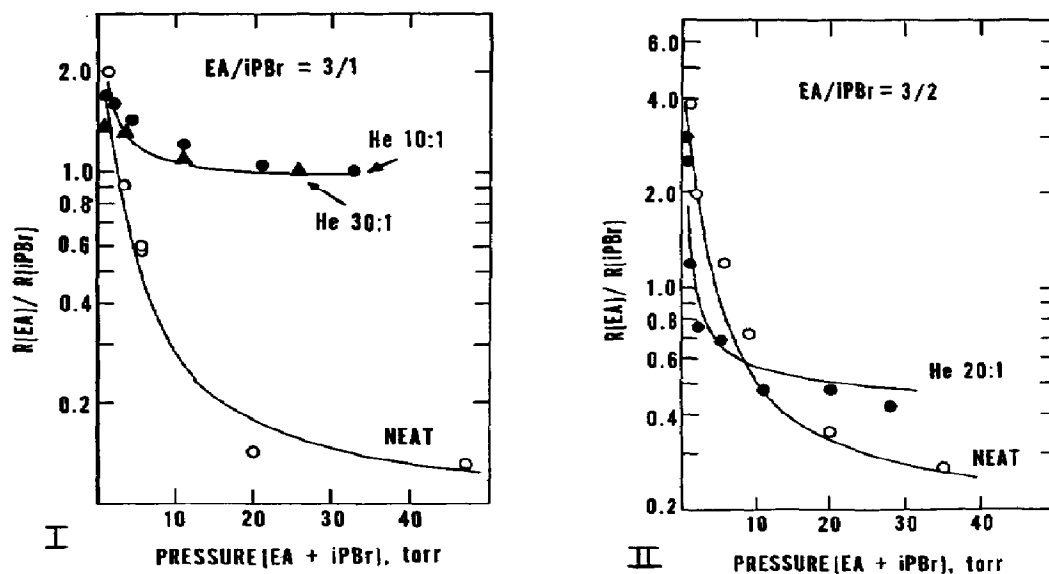


Fig. 1. Relative rates of decomposition of a 3:1 mixture of ethyl acetate and isopropyl bromide, neat and with added helium. The solid lines are based on model calculations (explained in text).

Fig. 2. Relative rates of decomposition of a 3:2 mixture of ethyl acetate and isopropyl bromide, neat and with added helium. The solid lines are based on model calculations.

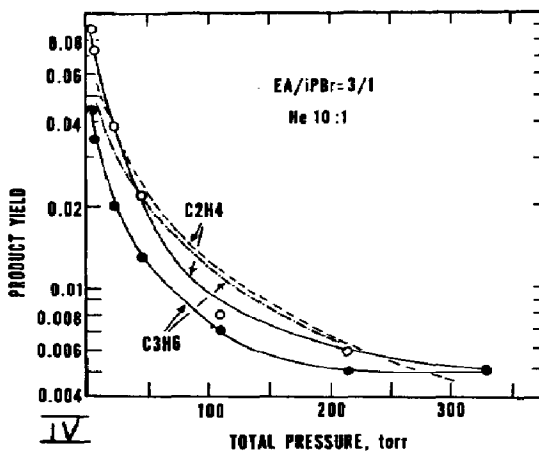
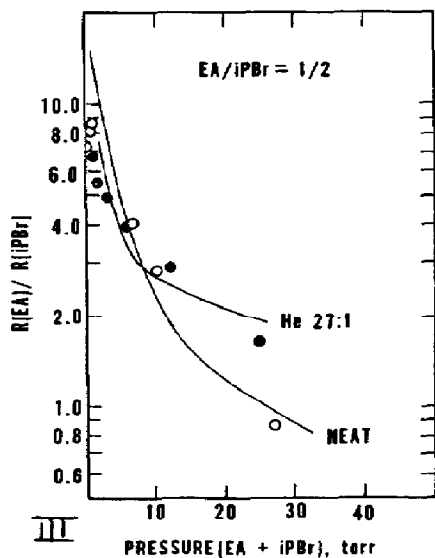


Fig. 3. Relative rates of decomposition of a 1:2 mixture of ethyl acetate and isopropyl bromide, neat and with added helium. The solid lines are based on model calculations.

Fig. 4. Absolute yields of products from the decomposition of a 3:1 mixture of ethyl acetate and isopropyl bromide with added helium. Solid lines are fits to experimental data, dashed lines are based on model calculations.

We have performed machine calculations using the above simple reaction scheme. The input data are summarized in Table 1 and the results are shown in figures 1-3 as the solid lines. While we can qualitatively represent the trends of the data quite well we cannot vary experimental conditions and simultaneously use a unique set of parameters. Values for k_t and k_d must be varied somewhat in order to achieve best fits. These variations however are never greater than a factor of 5. While this clearly points to inadequacies of the model, it is not unreasonable that so simple a representation does not lead to precise quantitative fits. While the shortcomings of such a model are apparent, the qualitative predictions are in good accord with the data. The model predicts fall-off curves of specificity vs. total pressure which follow very closely the experimental trends. The decrease in yield vs. pressures, figure 4, the least satisfactory fit, still roughly predicts the decay in yield with increasing pressure. The effect of added inert gas in preserving specificity (figures 1-3), is in excellent accord with the experimental findings. Also the concept of a bottleneck introduces an inherent disequilibrium which basically accounts for the persistent specificity at high total pressures.

TABLE 1
Rate constants* used for modeling specificities and products yields of Figs. 1 - 4

| (EA/iPBr)/He | k_{τ} ($\text{cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$) | k_d ($\text{cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$) |
|--------------|---|--|
| (3/1)/0 | 1.7×10^{-11} | 1.0×10^{-11} |
| (3/1)/10 | 1.8×10^{-11} | 2.2×10^{-11} |
| (3/1)/30 | 1.8×10^{-11} | 7.3×10^{-12} |
| (3/2)/0 | 1.2×10^{-11} | 2.0×10^{-11} |
| (3/2)/20 | 4.0×10^{-11} | 1.0×10^{-11} |
| (1/2)/0 | 4.0×10^{-12} | 4.0×10^{-12} |
| (1/2)/27 | 6.3×10^{-12} | 2.5×10^{-12} |

*Calculations are insensitive to the absolute values of k_p , k_r or k_r' . For all calculations we used $k_p = 8.3 \times 10^{-19}$, $k_p' = 0$, $k_r = 4.2 \times 10^{-19}$, and $k_r' = 8.3 \times 10^{-18}$, all in units of $\text{cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$.

The results of the present paper and the present two level bottleneck concept are in excellent agreement with the parallel calorimetric paper [3] which substantiates in a different, perhaps in a more direct way, that these ethyl acetate containing systems can be in severe thermal disequilibrium up to high total pressures.

References

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2. S. W. Benson and H. E. O'Neal, Kinetic Data on Unimolecular Reactions NSRDS-NBS-21, U. S. Government Printing Office (1970).
3. W. Braun, J. T. Herron, W. Tsang, and K. Churney, paper presented at this meeting by J. T. Herron.