

Figure 1. Excess static surface tensions γ_{at}^{E} as a function of mole fraction x_1 for (i) argon (1) + methane (2) at 90.7 K, (ii) carbon monoxide (1) + methane (2) at 90.7 K, (iii) nitrogen (1) + methane (2) at 90.7 K, and (iv) nitrogen (1) + argon (2) at 83.8 K; the upper full line gives the excess static surface tension from the van der Waals model setting $\rho = 0$ and the lower full line the excess surface tension from the same model but with both ξ and ρ taking the values which fit the bulk properties, for N₂ + Ar the two lines are indistinguishable: (**①**) experiment (ref 5).

the size cross-term parameter from the Lorentz or arithmetic-mean combining rule, was set equal to zero. We now report the effect on the surface tension predicted by the same monolayer model of assigning to ξ and ρ the simultaneous values found by Soares, Nieto de Castro, and Calado to give the best account of all the bulk properties, and particularly the excess volume, of the same mixtures by again using a van der Waals one-fluid model.² The results of the present and the previous calculations in terms of the excess static surface tension $\gamma_{\rm st}^{\rm E} = \gamma_{\rm st} - x_1\gamma_1 - x_2\gamma_2$ are shown in Figure 1.

The values of ξ found by Soares, Nieto de Castro, and Calado are slightly different from those used by Dickinson and McLure³ and they lead to very small changes in the predicted γ_{st}^{E} for $\rho = 0$ in the direction of improved prediction. For N₂ + Ar at 83.8 K the former ξ leads to agreement which is complete with $\rho = 0$ and which is unaltered by the introduction of the ρ which improves the fit of the excess volume. For the remaining mixtures, Ar + CH₄, CO + CH₄, and N₂ + CH₄, all at 90.7 K, γ_{st}^{E} previously predicted to be less negative than the measured value moves into closer accord when the deviation from the Lorentz rule is included in the calculation. For all four mixtures the incorporation of the fitted ξ and ρ leads to better reproduction of the skewness of the γ_{st}^{E} vs. x isotherm.

None of the foregoing affects the earlier conclusions regarding the general applicability of the first-order monolayer model of Prigogine and Defay⁴ for predicting $\gamma_{\rm st}^{\rm E}$ for simple mixtures. However, our results demonstrate that the success of a theory for surface tensions, just as for excess volumes, cannot be fairly assessed unless deviations from both the Berthelot and the Lorentz combining rules for the cross-term parameters are taken into account.

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Department of Chemistry The University Sheffield S3 7HF, United Kingdom

Centro de Química Estrutural Instituto Superior Tecnico Avenida Robisco País 1000 Lisbon, Portugal Virgilio A. M. Soares

Ian A. McLure*

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Formation of Vinylidenecarbene Intermediates in Multiple Infrared Photon Elimination Reactions

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Sir: Multiple infrared photon excitation (MIRPE) of α -chloro olefins (R₂C=CHCl) by intense CO₂ laser pulses has been found to lead to elimination of HCl.¹⁻³ Deuterium labeling studies² have shown that the reaction proceeds mainly via a 3-center elimination. This result suggests that vinylidenecarbene (R₂C=C:) may be formed during the dehydrohalogenation. Such species are well-known in solution;⁴ however, the only other gas-phase reaction in which they are formed appears to be mercury-photosensitized 1,1 eliminations.^{4,5} Carbenes, such as :CF₂, have often been observed in laser-induced multiple-photon dissociation.⁶

In the MIRPE of vinyl chloride (R = H, D), acetylene is the sole hydrocarbon product, suggesting that rearrangement of the carbene is extremely rapid, if not concerted with the elimination. This behavior is consistent with expectations^{4,7} that the barrier to the rearrangement

$$H_2C = C: \rightarrow HC = CH \tag{1}$$

is extremely low. We have extended our previous work² on these systems to substituted vinyl chlorides ($\mathbf{R} = CH_3$, F) in order to see whether the rearrangement could be slowed down sufficiently to permit the vinylidenecarbene to exist as a long-lived intermediate.

1-Chloro-2-methylpropene (Aldrich) and 2-chloro-1,1difluorethylene (PCR) were used as received except for transfer under reduced pressure to the reaction cell. Infrared spectra prior to MIRPE showed no major impurities to be present. The compounds were photolyzed with the 9.6- μ m P(16) or P(18) and 10.6- μ m R(18) CO₂ laser lines, respectively, either alone at pressures of 4–5 torr or in the presence of added gases. The gaseous product mixtures were collected and analyzed by GC/MS (H/P 5990 A or Hitachi RMU-61).

The MIRPE of $(CH_3)_2C$ —CHCl leads to HCl (observed in the product infrared spectrum) and butadiene as major products, with smaller amounts of allene, 2-butyne, and diacetylene. Photolysis in the presence of CH₃OH, H₂O, NH₃, H₂S, or D₂S vapor yielded no additional products. These results suggest that the $(CH_3)_2C$ —C: formed by loss of HCl rearranges extremely rapidly, either by methyl migration across the double bond (eq 2) or by intramolecular insertion (eq 3).

Since the acetylenic form is $\sim 30-40$ kcal/mol more stable than the carbene,⁷ the resulting 2-butyne, if formed, would contain a large amount of excess vibrational energy. Some of this could be stabilized by collisional relaxation,

$$\begin{array}{c} CH_{3} \\ CH_{3} \\ CH_{3} \\ \end{array} C = C: - CH_{3}C \equiv CCH_{3} - CH_{2} \equiv CHCH \equiv CH_{2} (2) \\ 0 \\ CH_{3} \\ CH_{$$

but the principal route seems to be further rearrangement to the still more stable butadiene. The same products could be derived from the methycyclopropene since the ring can open to form the butyne directly⁸ or the butadiene by way of the 2-carbene.⁹ A possible test of this proposed mechanism would be to deactivate collisionally these intermediates and quench further rearrangement by adding an inert buffer gas; it must be remembered, however, that increased collisions can also influence the MIRPE process itself^{1,3} and thus the mean excitation in the products. It may be noted that allene is also found when CF_2Cl_2 is photolyzed in the presence of $(CH_3)_2C=CH_2$ and results from secondary multiphoton excitation of $CH_3(CH_2)C=$ CH_{2} .⁶ Diacetylene appears to be a ubiquitous side product in reactions of this type.^{1,2,10}

The behavior of CF_2 —CHCl under the same conditions is quite different. Aside from HCl, the principal products are C_2F_4 (67%) and C_2F_3H (33%). No C_2F_2 is observed. In the presence of added H_2S or CH_3OH , the products are $C_2F_2H_2$ (82%),¹¹ C_2F_3H (12%), and C_2F_4 (6%). It seems clear that, in this system, the $F_2C==C$: species is long-lived, with essentially no rearrangement taking place to the acetylene. In the presence of labile hydrogens, the dominant reaction path seems to be H abstraction to form stable olefins. A possible mechanism to form the C_2F_4 would be secondary MIRPE of the vinylidenecarbene to form : CF_2 plus free carbon; a small amount of soot formation in the pure CF_2 =CHCl is consistent with this possibility. When the photolysis is carried out in the presence of D_2S , the principal product is C_2F_2HD , with a lesser amount of $C_2F_2D_2$ and small amounts of the previously mentioned products. The presence of $C_2F_2D_2$ confirms the existence of $F_2C=-C$;; the large amount of C_2F_2HD suggests that a C–Cl homolysis channel, to form C_2F_2H , is also important in this system.¹² The chemistry of this system is, indeed, quite complex, since several dissociation channels following MIRPE are available.

These results demonstrate that, not surprisingly, difluorovinylidene does not undergo rearrangement and can readily be trapped by hydrogen donors, whereas isobutylidene undergoes rearrangement more rapidly than it can be trapped. Since $(CH_3)_2C=C$: can be trapped in solution,⁴ the activation barrier to rearrangement must be no less than 10–15 kcal/mol or so. In the case of $H_2C==C$; Schaefer and co-workers¹³ have predicted a barrier to rearrangement 1 of 8.6 kcal/mol. For the rearrangement

$$F_2C = C: \rightarrow FC = CF \tag{4}$$

however, a semiquantitative MO calculation¹⁴ gives an activation barrier \sim 50-60 kcal/mol higher than that for

reaction 1. The greater vibrational complexity of $(CH_3)_2C=C$; as compared with $H_2C=C$: or $F_2C=C$; will lead to a partitioning of absorbed infrared energy into internal modes of the first-named species, thus providing sufficient energy to surmount the barrier.¹⁵ For the parent or difluoro species, the lower degree of vibrational excitation is sufficient to permit reaction 1 to occur, but not reaction 4, with its appreciably higher barrier.

This work illustrates how the MIRPE process may be of value in chemical investigations by permitting the preparation of primary dissociation products or unstable intermediates at a high instantaneous concentration in the presence of cold diluents. Spectroscopic characterization of species such as vinylidenecarbenes, which have hitherto not been directly observed, may be possible in this way.

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Department of Chemistry	Christopher Reise
Massachusetts Institute of Technology	Jeffrey I. Steinfeld
Cambridge, Massachusetts 02139	-

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