be formed.[10] Moreover, heterohelicenes like VIII are useful as starting materials for higher members of the series since they allow selective substitution in the terminal heterocyclic ring.

(10) S. D. Cohen, M. V. Mijovic, and G. A. Newman, *Chem. Commun.*, 722 (1968).

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On the Inadequacy of the "Chemical Method" to Determine Relative Quenching Cross-Section Values for Mercury $6(^3P_1)$ Atoms

Sir:

Quenching cross-section values (σ_Q^2) for Hg $6(^3P_1)$ atoms, interacting with a large number of compounds, have been determined by a chemical method developed by Cvetanović.[1,2] The results given below indicate that this method yields values for σ_Q^2 which are dependent upon the incident light intensity. The σ_Q^2 values for a given compound, as determined by the chemical method, will therefore depend upon the experimental conditions used. Thus the method will not provide a reliable σ_Q^2 value.

Values of I_a, the light absorbed per minute in the whole volume of the reaction cell, were determined by at least two different actinometries. The intensity of the incident light (I_{inc}) was calculated using the reaction cell surface which was exposed to the uv light.

Cvetanović,[1,2] from 2537-Å irradiation of RH–nitrous oxide mixtures, in the presence of mercury, showed that the variation of the reciprocal of the quantum yield of the nitrogen product ($1/\varphi_{N_2}$) with the ratio of the concentrations, (RH)/(nitrous oxide), is linear. The observations have been explained by the following simplified mechanism.

$$\mathrm{Hg} + h\nu \xrightarrow{2537\ \text{Å}} \mathrm{Hg}\ 6(^3P_1) \tag{1}$$

$$\mathrm{Hg}\ 6(^3P_1) + \mathrm{RH} \longrightarrow \mathrm{Hg}\ 6(^1S_0) + \mathrm{R} + \mathrm{H} \tag{2}$$

$$\mathrm{Hg}\ 6(^3P_1) + \mathrm{N_2O} \longrightarrow \mathrm{Hg}\ 6(^1S_0) + \mathrm{N_2} + \mathrm{O} \tag{3}$$

$$\mathrm{O} + \mathrm{RH} \longrightarrow \text{products} \tag{4}$$

$$\mathrm{H} + \mathrm{RH} \longrightarrow \text{products} \tag{5}$$

This neglects the formation of Hg $6(^3P_0)$ in the system. This mechanism has been used to relate the slope of the plot of $1/\varphi_{N_2}$ *vs.* (RH)/(N_2O) with the rate constant ratio k_2/k_3.

$$\frac{1}{\varphi_{N_2}} = 1 + \frac{k_2(\mathrm{RH})}{k_3(\mathrm{N_2O})} \tag{6}$$

Figures 1 and 2 however show that for a change in I_{inc} of 10^3, the slope of the straight line varies by a factor of 4.7 for *n*-butane and 1.3 for propylene. A variation in nitrogen quantum yield has also been reported for the diborane–nitrous oxide system.[3] Since the slope depends on the value of I_{inc}, it is unlikely that it represents k_2/k_3 exclusively. The fact that the variation in the slope is dependent upon the compound used renders the "chemical method" unreliable for the determination of σ_Q^2 values.

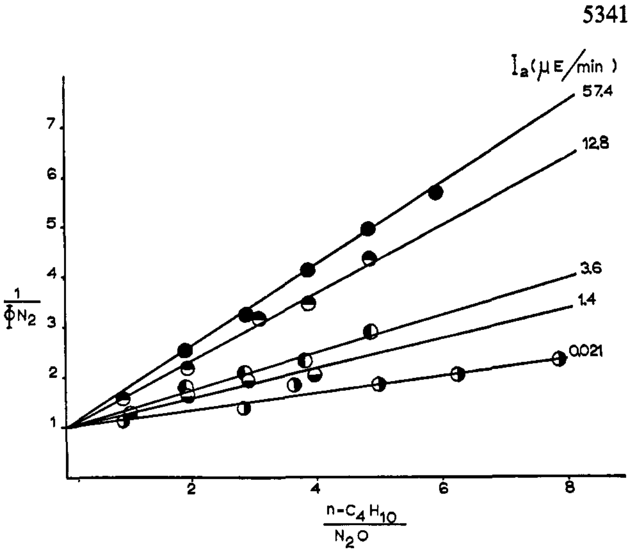

Figure 1. The variation of $1/\varphi_{N_2}$ with (*n*-butane)/(nitrous oxide) at different I_{inc}.

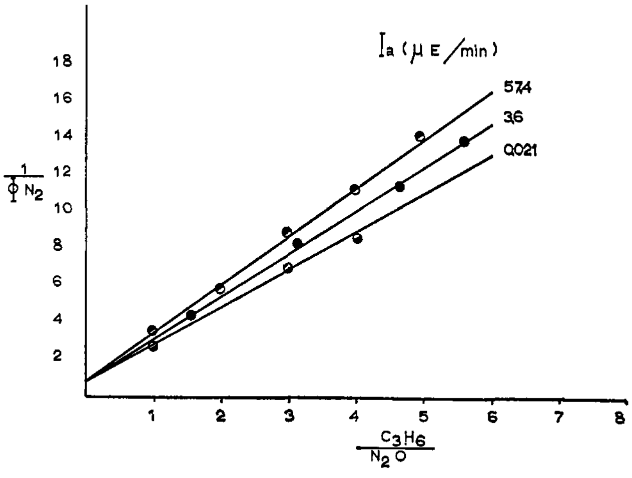

Figure 2. The variation of $1/\varphi_{N_2}$ with (propylene)/(nitrous oxide) at different I_{inc}.

The σ_Q^2 values, calculated using the equation

$$\frac{\sigma_1^2}{\sigma_2^2} = \frac{\beta_1}{\beta_2}\left(\frac{1 + M_{Hg}/M_2}{1 + M_{Hg}/M_1}\right)^{1/2} \tag{7}$$

where σ^2, β, and M represent the quenching cross-section value, the slope of the plot $1/\varphi_{N_2}$ *vs.* (RH)/(N_2O), and the atomic or molecular weight, respectively, and subscripts 1 and 2 refer to *n*-butane and propylene, respectively, are shown in Table I. The values indicate

Table I. Variation of the σ_Q^2 Values Calculated for Propylene with I_{inc}

I_{inc}, μEinsteins min^{-1} cm^{-2}	I_a, μEinsteins min^{-1}	β_1	β_2	σ_1^2, Å^2	σ_2^2, Å^2
1.12	57.4	0.80	2.8	3.6[a]	11.1
0.65	12.8	0.67	...		....
0.18	3.6	0.37	2.5		21.4
0.071	1.4	0.29	...		....
0.0011	0.021	0.17	2.2		40.8

[a] Reference standard.

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(1) R. J. Cvetanović, *J. Chem. Phys.*, **23**, 1208 (1955).

(2) R. J. Cvetanović, W. E. Falconer, and K. R. Jennings, *ibid.*, **35**, 1225 (1961).

(3) F. P. Fehlner and R. L. Strong, *J. Phys. Chem.*, **64**, 1522 (1960).

a constant increase in $\sigma_Q{}^2$ (C_3H_6) as I_{inc}'s decrease. The range of these values, 11.1–40.8 Å^2, may be compared with the literature values of 29.8–46 Å^2.[4]

The results shown here indicate that the mechanism previously proposed for the photodecomposition of N_2O–*n*-butane mixtures is incomplete, and hence values of $\sigma_Q{}^2$ based on this mechanism may be in error. It is possible that radical–radical reactions are responsible for the variations in these slopes. If this is the case, reliable $\sigma_Q{}^2$ values would be obtained only at very low I_{inc}, and the chemical method would be applicable only under this restricted condition. Further work is now in progress to determine a more complete mechanism and to find the specific conditions necessary for the evaluation of reliable $\sigma_Q{}^2$ values.

[4] J. N. Pitts, Jr., and J. G. Calvert, "Photochemistry," John Wiley and Sons, Inc., New York, N. Y., 1966, p 75.

[5] (a) Holder of a postgraduate "Hydro-Québec" scholarship; (b) to whom inquiries should be addressed.

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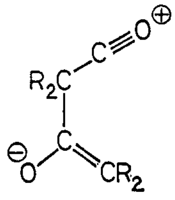
The Mechanism of Dimerization of Dimethylketene

Sir:

The structure of ketene dimers has been elucidated, but not the mechanism of their formation. While ketene itself dimerizes to γ-methylene-β-propiolactone, its substituted derivatives furnish predominantly or exclusively cyclobutane-1,3-diones as head-to-tail dimers. The mutual interconversion of the β-lactone- and the cyclobutanedione-type dimers by electrophilic or nucleophilic catalysts[1] needs only the cleavage of one bond. This suggested the zwitterion I with its good charge stabilization as a possible intermediate in the dimerization process.[2,3] Hoffmann and Woodward[4] pointed out that the dimerization of ketenes does not obey the selection rules for concerted processes and must proceed through a multistep reaction.



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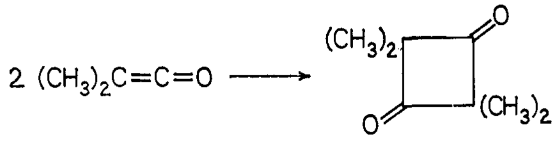


II III

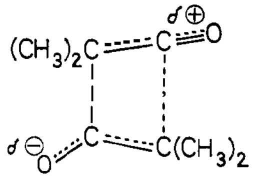
We have investigated the solvent dependence of the dimerization rate constant of dimethylketene and found the results incompatible with the formation of a zwitterionic intermediate in the rate-determining step. The six-proton singlet in II and the twelve-proton singlet in III (at τ 8.35 and 8.66, respectively, in $CDCl_3$) allowed a rather precise nmr analysis; dimerization of II was followed up to 80–90% and obeyed strictly second-order kinetics. The rate constants in seven solvents (Table I) display a moderately good linear correlation with the empirical parameter of solvent polarity, E_T.[5] The total range of solvents produced changes in the rate constants of only a factor of 30.

Table I. Rate Constants for the Dimerization of Dimethylketene in Various Solvents at 35°

Solvent	10^5k_2, l mol^{-1} sec^{-1}	E_T, kcal mol^{-1} [a]
CCl_4	2.31	32.5
C_6H_6	4.42, 4.79	34.5
C_6H_5Cl	6.25, 6.73	37.5
$CDCl_3$	23.6, 23.9	39.1
CH_2Cl_2	25.4, 26.9	41.1
C_6H_5CN	35.0, 34.8	42.0
CH_3CN	65.7, 69.2	46.0

[a] K. Dimroth, C. Reichardt, T. Siepmann, and F. Bohlmann, *Ann.*, **661**, 1 (1963).

The formation of a zwitterion should be facilitated much more by an increase of solvent polarity.[6] The cycloaddition of tetracyanoethylene with 4-methoxystyrene shows a solvent dependence of nearly 10^5,[7] the quaternization of tripropylamine with methyl iodide also a spread of 10^5,[8] and the addition of piperidine to methyl propiolate one of 10^3.[9]



IV

The dipole moment of dimethylketene (1.9 D. in benzene[10]) vanishes in the dimer III. One should expect a slightly reverse effect of solvent polarity on k_2 if a symmetrical transition state occurred. We conclude, therefore, unequal bond formation and partial charge separation in the transition state IV. This is possibly in accordance with a modification of the selection rules[11] which allows 2 + 2 cycloadditions of cumulated systems to be concerted.

Kinetic measurements at different temperatures gave the following Eyring parameters for the dimerization

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[1] D. G. Farnum, J. R. Johnson, R. E. Hess, T. B. Marshall, and B. Webster, *J. Am. Chem. Soc.*, 87, 5191 (1965), and earlier papers.

[2] J. D. Roberts and C. M. Sharts, *Org. Reactions*, **12**, 26 (1962).

[3] R. Huisgen, R. Grashey, and J. Sauer in "The Chemistry of Alkenes," S. Patai, Ed., John Wiley & Sons, Inc., New York, N. Y., 1964, p 790.

[4] R. Hoffmann and R. B. Woodward, *J. Am. Chem. Soc.*, 87, 2046 (1965).

[5] See Table I, footnote *a*.

[6] A preequilibrium of II with a zwitterionic intermediate could lead to counterbalancing solvent effects on equilibrium and rate of ring closure. However, the reversibility of zwitterion formation is not very probable.

[7] D. W. Wiley, E. I. du Pont de Nemours and Co., Wilmington, Del., private communication.

[8] J. C. Jungers, L. Sajus, I. de Aguirre, and D. Decroocq, *Rev. Inst. Franc. Petrole Ann. Combust. Liquides*, 21, 109, 137 (1966).

[9] B. Giese and R. Huisgen, *Tetrahedron Letters*, 1889 (1967).

[10] C. L. Angyal, G. A. Barclay, A. A. Hukins, and R. J. W. LeFèvre, *J. Chem. Soc.*, 2583 (1951).

[11] We thank Professor R. B. Woodward, Harvard University, for a private communication.