a constant increase in σ_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 σ_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 σ_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 σ_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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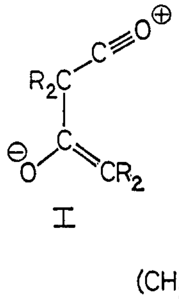
The Mechanism of Dimerization of Dimethylketene

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.



I

II III

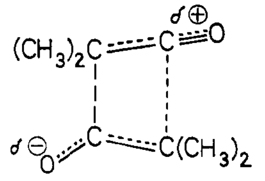
We have investigated the solvent dependence of the dimerization rate constant of dimethylketene and found the results incompatible with the formation of a zwitterionic intermediate in the rate-determining step. The six-proton singlet in II and the twelve-proton singlet in III (at τ 8.35 and 8.66, respectively, 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. Le-Fèvre, *J. Chem. Soc.*, 2583 (1951).

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

of II in benzonitrile: $\Delta H^{\ddagger} = 10.8$ kcal mol^{-1} and $\Delta S^{\ddagger} = -42$ eu. Large negative activation entropies are consistent with highly ordered transition states.

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Fully Fluorinated Alkoxides. III. Perfluoropinacol, a Useful Bidentate Ligand

Sir:

The perfluoropinacol molecule, $(CF_3)_2C(OH)C(OH)(CF_3)_2$, is known to form the basis of a number of five-membered heterocycles of type $\overline{OC(CF_3)_2C(CF_3)_2OM}$, where the element M is Si,[1] Ge, Sn, B, or S.[2]

Previously reported compounds of this type have been made by the reaction of the appropriate dihalides with the ionic alkoxides of perfluoropinacol in anhydrous donor solvent, such as tetrahydrofuran. However, the stability of perfluoropinacol in water, combined with its acidic nature (pK = 5.95[3]), suggests that it should be possible to prepare complexes in which the pinacol ion is acting as a bidentate ligand to a metal ion.

This we have found to be the case, and we now report that stable complexes with a variety of metals may readily be made in aqueous solution. Complex ions of the type $[M(PFP)_3]^{3-}$, where PFP represents the perfluoropinacolato ion, $[OC(CF_3)_2C(CF_3)_2O]^{2-}$, have been made where M = Fe^{3+} or Al^{3+}, while complexes of the type $[M(PFP)_2]^{2-}$ are formed where M = Mn^{2+}, Ni^{2+}, Cu^{2+}, or Zn^{2+}.

The most general method of preparation was to add the aqueous metal ion (as the metal sulfate) to the calculated amount of perfluoropinacol in a 1:1 methanol/water mixture (the pinacol having only limited solubility in water). No reaction was observed, but the introduction of aqueous potassium hydroxide produced immediate color changes in those solutions which were colored, and, by addition of base to a pH of about 7.5, the complex ions were formed according to the equation

$$nH_2PFP + M^{n+} + 2nOH^- \longrightarrow [M(PFP)_n]^{n-} + 2nH_2O$$

where n = 2 or 3.

In some cases, *e.g.*, iron and manganese, it was possible to prepare the complex ions by dissolving the freshly precipitated metal hydroxide in partially neutralized pinacol

$$3H_2PFP + Fe(OH)_3 + 3OH^- \longrightarrow [Fe(PFP)_3]^{3-} + 6H_2O$$

but this route was not suitable for all the metals studied.

Solid products were obtained by filtration of the above solutions to remove any metal hydroxides, followed by crystallization by evaporation at 25° of aqueous or methanolic solutions and drying at 25° *in vacuo*. The following compounds were characterized.

Potassium tris(perfluoropinacolato)ferrate(III) deposited as very pale yellow crystals from water. *Anal.* Calcd for $C_{18}F_{36}O_6FeK_3$: C, 18.49; F, 58.50. Found: C, 18.36; F, 58.38; magnetic moment, 6.0 BM.

Potassium tris(perfluoropinacolato)aluminate(III) deposited as colorless crystals from water. *Anal.* Calcd for $C_{18}F_{36}O_6AlK_3$: C, 18.95; F, 59.97. Found: C, 19.03; F, 59.54.

Potassium bis(perfluoropinacolato)manganate(II) formed brown crystals from water, dehydrating *in vacuo* to a pale yellow solid. *Anal.* Calcd for $C_{12}F_{24}O_4MnK_2$: C, 18.08; F, 57.20; Mn, 6.89. Found: C, 18.12; F, 57.02; Mn, 6.85; magnetic moment, 5.2 BM.

Potassium bis(perfluoropinacolato)nickelate(II) formed a yellow aqueous solution giving purple crystals of a dihydrate, dehydrating *in vacuo* to deep blue-purple anhydrous compound (diamagnetic). *Anal.* Calcd for $C_{12}F_{24}O_4NiK_2$: C, 17.99; F, 56.93; Ni, 7.33. Found: C, 17.56; F, 56.71; Ni, 7.28.

Potassium bis(perfluoropinacolato)cuprate(II) formed a deep blue aqueous solution giving deep blue crystals of stable dihydrate. *Anal.* Calcd for $C_{12}H_4F_{24}O_6CuK_2$: C, 17.12; H, 0.48; F, 54.16; Cu, 7.55. Found: C, 16.92; H, 0.64; F, 54.10; Cu, 7.61; magnetic moment, 2.0 BM.

Potassium bis(perfluoropinacolato)zincate(II) deposited as colorless crystals from water. *Anal.* Calcd for $C_{12}F_{24}O_4ZnK_2$: C, 17.84; F, 56.46. Found: C, 17.88; F, 56.49.

A brief investigation was made of some complexes containing other cations. When perfluoropinacol was added to an aqueous stirred suspension of iron(III) hydroxide and silver oxide, reaction occurred to give silver tris(perfluoropinacolato)ferrate(III), as pale yellow crystals from water, rapidly darkening on exposure to light. *Anal.* Calcd for $C_{18}F_{36}O_6FeAg_3$: C, 15.71; F, 49.72. Found: C, 15.65; F, 49.60.

Metathetical reaction of the aqueous silver salt with aqueous tris(ethylenediamine)cobalt(III) iodide gave tris(ethylenediamine)cobalt(III) tris(perfluoropinacolato)ferrate(III), $[Co(en)_3][Fe(PFP)_3]$. *Anal.* Calcd for $C_{24}H_{24}F_{36}O_6N_6CoFe$: C, 22.32; H, 1.87; F, 52.97; N, 6.51. Found: C, 22.01; H, 2.08; F, 52.68; N, 6.18.

The cesium salts appeared to be much less soluble than the potassium salts. With the bis(perfluoropinacolato)cuprate(II), for example, addition of aqueous cesium chloride to an aqueous solution of the potassium salt gave an immediate precipitate of the deep blue cesium salt, which was then recrystallized from methanol. *Anal.* Calcd for $C_{12}F_{24}O_4CuCs_2$: C, 14.51; F, 45.89. Found: C, 14.45; F, 45.62.

In the iron and aluminum compounds described above, where the metal atom is chelated by three pinacol ligands, there is no reason to doubt that the structure is basically octahedral, similar to the well-known trioxalatoferrate or -aluminate ions, and the magnetic moment of the iron complex is that to be expected from a high-spin d^5 species. Similarly, the magnetic moment of the ion $[Cu(PFP)_2]^{2-}$ is within the range usually found for d^9 species of copper(II), and that of the ion $[Mn(PFP)_2]^{2-}$ is consistent with d^5 manganese(II). With the nickel complex $[Ni(PFP)_2]^{2-}$, the diamagnetism would suggest a square-planar configuration, but more detailed interpretations of the structures of all these

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(1) C. L. Frye, R. M. Salinger, and T. J. Patin, *J. Am. Chem. Soc.*, **88**, 2343 (1966).

(2) M. Allan, A. F. Janzen, and C. J. Willis, *Chem. Commun.*, 55 (1968).

(3) W. J. Middleton and R. V. Lindsey, *J. Am. Chem. Soc.*, **86**, 4948 (1964).