Table II. Yields of Products from Reaction of Triplet Acetone, Generated by TMD Thermolysis, with Solvent[a]

| Solvent[b] | Reaction time, hr | Temp, °C | A<br>Acetone,[c] % | B<br>Benzene,[c] % | C<br>2-Propanol[c] + radical coupling products,[c] % |
|---|---|---|---|---|---|
| 1,4-Cyclohexadiene[d] | 2 | 70 | 90 | 7.5 ± 0.5 | 10 ± 1[e] |
| 1,4-Cyclohexadiene–$CH_2Cl_2$ (3:2) | 2.5 | 55 | 96 | 2 ± 1 | 3.5 ± 1 |
| 1,4-Cyclohexadiene–$CH_2Cl_2$ (4:1) | 2.5 | 55 | 93 | 6.5 ± 1 | 7.5 ± 1 |
| 1,4-Cyclohexadiene–methanol (4:1) | 2 | 55 | 100 | None observable<br><0.5 | None observable<br><1 |

[a] All reactions were carried out in sealed, degassed, nmr tubes. [b] Concentration of TMD in neat 1,4-cyclohexadiene is 0.25 *M;* in all other experiments, [TMD] is 0.2 *M*. [c] Analysis of solution on Varian T-60 nmr: 1,4-cyclohexadiene, $\delta$ 2.7, 5.7; acetone, $\delta$ 2.1; benzene, $\delta$ 7.3; 2-propanol, $\delta$ 1.1, 1.2; 2-(2,4-cyclohexadienyl)-2-propanol, $\delta$ 1.18; pinacol, $\delta$ 1.2. A + C taken as 100%. [d] The 1,4-cyclohexadiene (Eastman) was purified by vpc and was benzene free. [e] 2-Propanol: 7.5 ± 0.5%

fluorescence of DBA has an activation energy of −4 kcal, $E_a$, the activation energy of the luminescent decomposition of TMD, is equal to 4 + $E_{\mathrm{Chl}}$, the activation energy derived from the luminescence intensities at the two temperatures. From the figures in Table I it can be seen that the activation energies of the *chemiluminescent* decomposition path are reproducible, are the same with and without fluorescer added, and are not significantly different in the alcohols from their values in benzene. This is in contrast with the reported much lower values for the *overall* activation energies in alcohols from an Arrhenius treatment.[2] The latter, of course, are based on total decomposition rates of the dioxetane.

A striking characteristic of the rates in methanol and ethanol is their irreproducibility. In discussing this point with Professor W. H. Richardson[9] of San Diego State University, we learned of the observation in his laboratory that ethylenediaminetetraacetic acid (EDTA) strongly retards certain dioxetane decompositions. We have subsequently found that various treatments can lower the rate of dioxetane decomposition in methanol by the following factors: standing over Chelex 100 for 1 day, ~10; passing through a Chelex 100 column, or distilling from disodium EDTA, ~20; standing with a large amount of Chelex 100 for 4 days, ~100; reacting solution made 5 × $10^{-4}$ *M* in disodium EDTA, ~250. The ratio of extreme rates was 116 for ethanol and 1.6 for benzene. The lowest rate constants thus far observed were the same within 15% in these three solvents (3.9 ± 0.6 × $10^{-5}$ $\mathrm{sec}^{-1}$ at 57°);[10] the luminescence intensities and therefore the quantum yields were also the same.

The effectiveness of disodium EDTA and the sequestering resin Chelex 100 in lowering the catalyzed rates indicates that these accelerations are due not to the alcohols but to trace impurities, probably of transition metal compounds. This catalytic effect explains a previously observed rapid decomposition of the dioxetane in the metal cavity of a microwave spectrometer.[11] The addition of cupric chloride in a concentration of $10^{-5}$ *M* increased by a factor of ~100 the rate of TMD decomposition in methanol distilled from disodium EDTA. Even dipping a copper wire in benzene increased the TMD decomposition in that solvent tenfold!

A dark catalytic pathway is also supported by the following results. When TMD is thermolyzed in degassed 1,4-cyclohexadiene as solvent, products attributable to hydrogen abstraction by triplet acetone are found (Table II). In mixed, degassed cyclohexadiene and untreated methanol (4:1, v/v), the yield of H-abstraction products is sharply decreased relative to that in mixed, degassed cyclohexadiene–methylene chloride (4:1, v/v). This indicated that the catalyzed decomposition reduced the overall yield of excited acetone from TMD by a mechanism other than dilution of the diene.

Because excited acetone rapidly attacks TMD, the reaction in degassed benzene free of H donors acquires chain character and, at high dioxetane concentration, follows second-order kinetics, though having been of first order in the presence of oxygen. The rapid reaction of 1 *M* TMD in untreated methanol is not appreciably affected in rate nor in order by removal of oxygen. This is independent evidence that no excited acetone is produced by the catalytic decomposition of TMD in untreated alcohol.

Further work on the nature of this catalysis is actively in progress.

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[9] W. H. Richardson, personal communication.

[10] Benzene untreated, ethanol with $10^{-4}$ *M* disodium EDTA, and methanol with 5 × $10^{-4}$ *M* disodium EDTA.

[11] W. E. Steinmetz, private communication.

## A Computer-Assisted Analysis of the Camphor-$^{14}C$ Sulfuric Acid Reaction.[1] Is 3,2-Endo Hydroxyl Shift Necessary?

*Sir:*

We have devised a computer program[2] which allows

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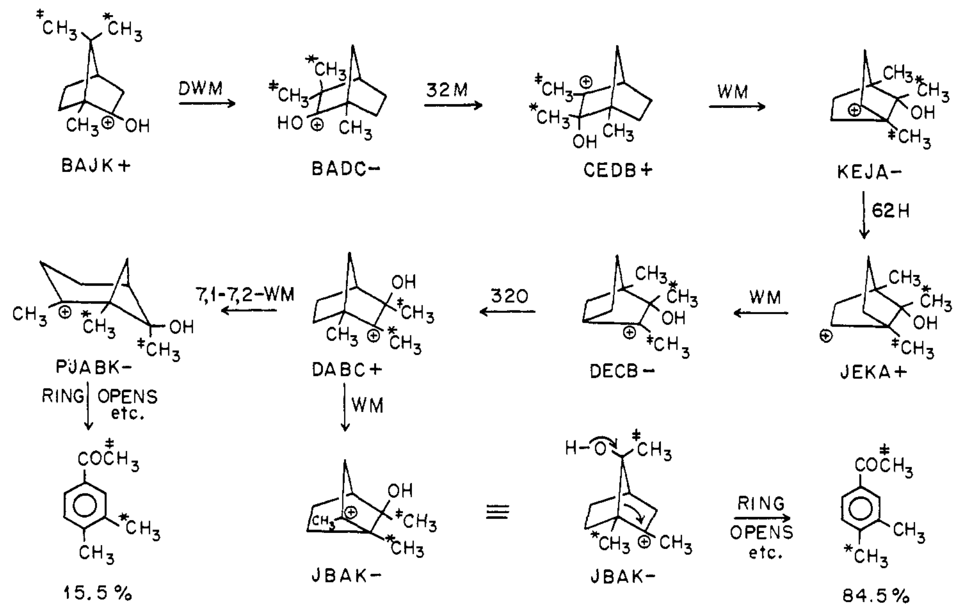
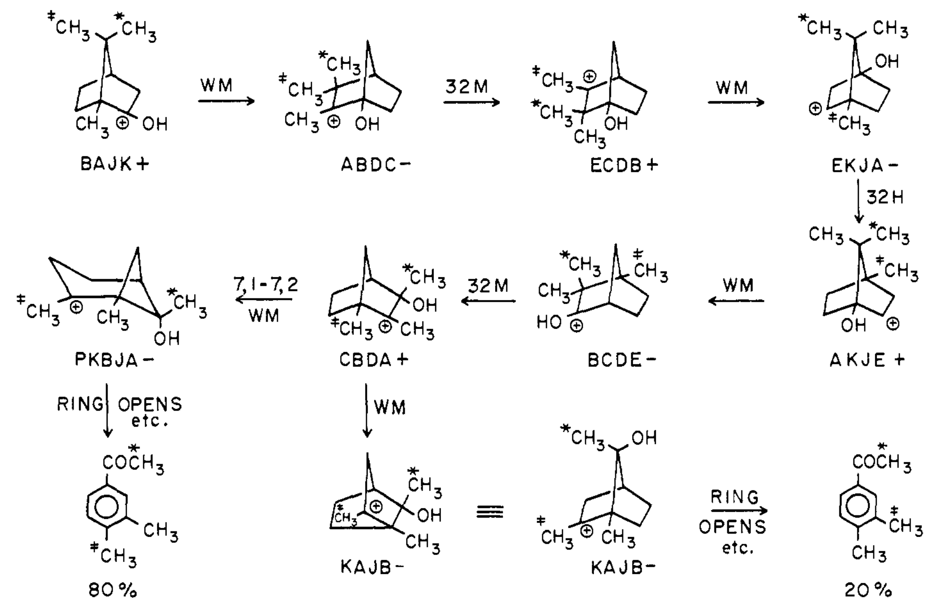
[1] This research was sponsored by the U. S. Atomic Energy Commission under contract with the Union Carbide Corporation.

[2] The method is based on permutations of the 11 letters A–K which describe specific positions on the 2-bicyclo[2.2.1]heptyl cation as follows: 1 = A; 2 = B; endo 3 = C; exo 3 = D; 4 = E; endo 5 = F; exo 5 = G; endo 6 = H; exo 6 = I; syn 7 = J; anti 7 = K. An abbreviated notation containing $n + 1$ characters represents any

**Scheme I.** Computer-Deduced Scheme for 90% Overall Contribution to the Rearrangement[3] of Camphor-$^{14}C_2$



**Scheme II.** Computer-Deduced Scheme for 10% Overall Contribution to the Rearrangement[3] of Camphor-$^{14}C_2$



us to enumerate all of the intermediates possible through the several processes substituted bicyclo[2.2.1]heptyl cations are known to undergo, which keeps track of isotopic labels and prints out the pathways connecting the intermediates. This program has been applied to the reaction of $^{14}C$-labeled camphor[3,4] with sulfuric acid to yield 3,4-dimethylacetophenone. The results of Rodig and Sysko[3] are given in Figure 1 and were explained by these[4] authors in terms of a complicated series of competing pathways, the most important of which, from protonated camphor, involves the fol-

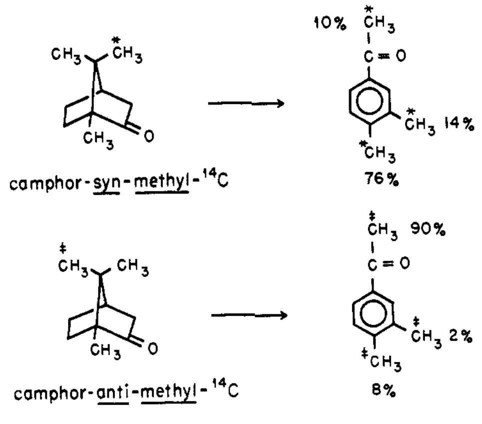


Figure 1. The results of Rodig and Sysko[3] in the $H_2SO_4$-catalyzed rearrangement of two labeled forms of camphor to 3,4-dimethylacetophenone. The percentages have been rounded off.

configuration of *n* substituents on one enantiomer (+) or its mirror image (−). Thus, protonated (+)-camphor becomes in our notation BAJK+, in which B fixes the position of the hydroxyl and AJK fix the positions of the three methyl groups. Protonated (−)-camphor becomes BAJK−. The appropriate symbols are employed in Schemes I and II, where the order of appearance of the last three letters specifies the carbon-14 labels. The symbol PJABK− in Scheme I signifies that the structure is a *precursor* (P) of JABK−, to which it is converted by a Wagner–Meerwein rearrangement. The program and notation will be described in detail in a forthcoming paper.

[3] O. R. Rodig and R. J. Sysko, *J. Amer. Chem. Soc.*, **94**, 6475 (1972).

[4] See also R. P. Lutz and J. D. Roberts, *ibid.*, **84**, 3715 (1962), who studied the reaction of fenchone-$^{14}C_2$ with sulfuric acid.

lowing rearrangements: (1) 7,1–7,2 "double Wagner–Meerwein" (DWM);[5] (2) 6,1–6,2 Wagner–Meerwein (WM); (3) Nametkin (32M);[6] (4) 3,2-endo hydroxyl; (5) 6,1–6,2 Wagner–Meerwein (WM),[5] and, finally, ring opening and dehydrogenation. One process in the foregoing mechanism has never been observed, namely the 3,2-endo shift of hydroxyl,[7,8] and Rodig and Sysko expressed considerable doubt concerning its validity. Rationalizing the data[3] is difficult, in that there are several thousand possible intermediates, whose enumeration and subsequent untangling by conventional methods is a formidable task. We have therefore applied our program[2] to the rearrangement of protonated camphor (Figure 1),[3] permitting WM, DWM, 6,2-hydride (62H),[9] 32H,[7] 32M (Nametkin),[6] and 3,2-exo hydroxyl (32O) shifts. No endo migrations were allowed. The results are illustrated in Scheme I (whose scheme contributes 90% to the overall reaction) and in Scheme II (10% contribution). The mechanism offered by these two schemes is completely consistent with the isotopic data,[3] is simpler than the explanations which were previously[3,4] proposed, and requires no endo migrations. When either DWM or 32O were omitted from the program, there were no satisfactory explanations for the results. Because of the thousands of intermediates possible in the rearrangement[3] of camphor-$^{14}C_2$ in sulfuric acid, the true situation could be more complicated than indicated by Schemes I and II. For example, we certainly cannot rule out some redistribution of carbon-14 between the 7-syn and the bridgehead methyl by the mechanism[10] proposed earlier for camphor racemization. In this connection it is interesting that even with DWM and 32O, we could not improve on these earlier mechanisms for the racemization of camphor[10] and fenchone.[3]

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[5] O. Aschan, *Justus Liebigs Ann. Chem.*, **838**, 1 (1911); H. Meerwein and K. van Emster, *Ber. Deut. Chem. Ges.*, **53**, 1825 (1920); **55**, 2521 (1922); J. Bertram and J. Helle, *J. Prakt. Chem.*, **61**, 293 (1900); D. S. Noyce, *J. Amer. Chem. Soc.*, 72, 924 (1950); O. Wallach, *Justus Liebigs Ann. Chem.*, **362**, 181 (1908); W. Hückel and H. Wolwoski, *Chem. Ber.*, **80**, 39 (1947); P. Yates and R. J. Crawford, *J. Amer. Chem. Soc.*, **88**, 1561 (1966); W. Hückel and H.-J. Kern, *Justus Liebigs Ann. Chem.*, **728**, 49 (1969) (who first observed the DWM by isolation of borneol on deamination of *endo*-fenchylamine); C. J. Collins, B. M. Benjamin, V. F. Raaen, I. T. Glover, and M. D. Eckart, *ibid.*, **739**, 7 (1970); and C. J. Collins and B. M. Benjamin, *J. Org. Chem.*, 37, 4358 (1972).

[6] S. S. Nametkin and L. Brüssoff, *Justus Liebigs Ann. Chem.*, **459**, 144 (1927); *J. Prakt. Chem.*, [2] **135**, 155 (1932).

[7] 3,2-Endo shifts in general are inhibited in 2-bicyclo[2.2.1]heptyl compounds; see, *e.g.*, C. J. Collins, Z. K. Cheema, R. G. Werth, and B. M. Benjamin, *J. Amer. Chem. Soc.*, **86**, 4913 (1964); P. v. R. Schleyer, *ibid.*, **89**, 701 (1967). The only documented examples of 3,2-endo hydride shifts are for severely restricted structures containing geminal methyl groups in the 7 position: A. W. Bushell and P. Wilder, Jr., *ibid.*, **89**, 5721 (1967); P. Wilder, Jr., and W. C. Hsieh, *J. Org. Chem.*, **36**, 2552 (1971).

[8] In the epoxidation of norbornene, H. C. Brown, W. J. Hammar, J. H. Kawakanie, S. Rothberg, and D. L. Vander Jagt (*J. Amer. Chem. Soc.*, **89**, 6381 (1967)) report the formation of 99.5% of the exo product and only 0.5% of the endo.

[9] N. J. Toivonen, *Suom. Kemistilehti B*, **24**, 62 (1951); W. E. Doering and A. R. Wolf, *Perfum. Essent. Oil Rec.*, **42**, 414 (1951); J. D. Roberts, C. C. Lee, and W. H. Saunders, Jr., *J. Amer. Chem. Soc.*, **76**, 4501 (1954).

[10] A. M. T. Finch, Jr., and W. R. Vaughan, *ibid.*, **91**, 1416 (1969); T. Miki, M. Nishikawa, and P. H. Hagiurara, *Proc. Jap. Acad.*, **31**, 718 (1955).

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## Basic Strength of Acetic Acid and $K^{f}_{IH^+}$ Values of Some Hammett Indicators in Acetonitrile

*Sir:*

In an early study,[1] we employed a solution of perchloric acid in anhydrous acetic acid for the determination of $K^{f}_{IH^+}$ values of three Hammett indicators in acetonitrile (AN). Reference[2,3] was made to the fact that perchloric acid was added in the form of protonated acetic acid–perchlorate ion pair $CH_3COOH_2^+ClO_4^-$. It was tacitly assumed that AN is a stronger base than acetic acid and that reaction 1 is virtually

$$CH_3COOH_2^+ClO_4^- + CH_3CN \rightleftharpoons CH_3CNH^+ (H_s^+) + ClO_4^- + CH_3COOH \quad (1)$$

instantaneous and quantitative.

Recently, Kinugasa *et al.*,[4] found that pure perchloric acid in a freshly prepared solution in AN is a relatively weak acid and that addition of acetic acid greatly increases the conductance of such a solution. Their results cast some doubt on the correctness of our values[1] of $K^{f}_{IH^+}$ of 2-nitroaniline (and the two other Hammett indicators). Since the calibration of the glass electrode for $pa_H$ measurements in AN[5] was based in part on the value of $K^{f}_{IH^+}$ of 2-nitroaniline (2-NA), the previously reported value[1] has been redetermined in acetic acid free methanesulfonic acid and recalculated in perchloric acid, taking the effect of acetic acid into account. In order to do this we have determined $K^{f}_{CH_3COOH_2^+}$ by measuring $[IH^+]/[I]$ of 2-nitro-4-chloroaniline (2-N-4ClA) and 2-nitro-4,5-dichloroaniline (2-N-4,5Cl$_2$A) in solutions of perchloric acid in AN containing various concentrations of acetic acid. Perchloric acid was added as 0.485 *M* solution in acetic acid. Extrapolation of $[IH^+]/[I]$ to zero concentration of acetic acid yielded $K^{f}_{IH^+}$. In separate experiments it was found that formation of $I \cdot HOOCCH_3$ and $IH^+ \cdot CH_3COOH$ is negligible. An example of the estimation of $K^{f}_{IH^+}$ of 2-N-4ClA and $K^{f}_{CH_3COOH_2^+}$ is given in Table I.

Table I. Determination of $K^{f}_{IH^+}$ of 2-Nitro-4-chloroaniline (I) and of $K^{f}_{CH_3COOH_2^+}$ in Perchloric Acid

| [HAc], *M* | $[IH^+]/[I]$ | $[IH^+]$, $M \times 10^4$ | $[H_s^+]$,[c] $M \times 10^4$ | $[CH_3COOH_2^+]$, $M \times 10^4$ | $K^{f}_{CH_3COOH_2^+}$[b] |
|---|---|---|---|---|---|
| 0 | (13.0)[a] | 1.23 | | | |
| 0.0244 | 10.$_0$ | 1.23 | 3.7 | | |
| 0.0694 | 7.$_1$ | 1.16 | 3.5 | 1.5 | (6.4) |
| 0.108 | 5.$_1$ | 1.12 | 2.6 | 2.6 | 9.3 |
| 0.198 | 3.$_1$ | 1.02 | 1.5 | 3.7 | 11.2 |
| 0.256 | 2.$_4$ | 0.95 | 1.2 | 4.1 | 13.0 |
| 0.412 | 1.$_7$ | 0.84 | 0.8$_3$ | 4.6 | 13.1 |
| 0.474 | 1.$_3$ | 0.75 | 0.6$_3$ | 4.9 | 16.0 |
| | | | | | Av 12 |

[a] Extrapolation yields log $K^{f}_{IH^+} = 4.3$. [b] An average value of log $K^{f}_{IH^+} = 4.2$ (see Table II) was used to calculate $K^{f}_{CH_3COOH_2^+}$. [c] $C_I = 1.35 \times 10^{-4}$ *M*; $C_{HClO_4} = 6.26 \times 10^{-4}$ *M*.

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[1] I. M. Kolthoff, S. Bruckenstein, and M. K. Chantooni, Jr., *J. Amer. Chem. Soc.*, **83**, 3927 (1961).

[2] S. Bruckenstein and I. M. Kolthoff, *J. Amer. Chem. Soc.*, **78**, 2974 (1956).

[3] I. M. Kolthoff and S. Ikeda, *J. Phys. Chem.*, **65**, 1020 (1961).

[4] M. Kinugasa, K. Kishi, and S. Ikeda, *J. Amer. Chem. Soc.*, in press.

[5] I. M. Kolthoff and M. K. Chantooni, Jr., *J. Amer. Chem. Soc.*, 87, 4428 (1965).