In the specific case $\lambda = 0$; $t_{l}^{r} = t_{*}^{o}$. In the case of a linear isotherm under the conditions of sorption from an unrestricted volume $t_{l}^{l} = \alpha_{o}b^{2}/6D_{i}c_{oo}$ [1].

CONCLUSIONS

1. The problem of the adsorption rate from a constant restricted volume for a granule of a monoporous adsorbent as a sheet is discussed for the case of a sharply convex isotherm, which is characteristic for microporous adsorbents.

2. Cases of both infinitely large and finite mass-exchange coefficient were analyzed.

3. A quite simple approximate analytical solution of this problem was obtained, which can be used to interpret experiments on the sorption rate on microporous adsorbents employing the gravimetric method and the method of x-raying a granule of the sorbent during the sorption of x-ray contrast materials.

LITERATURE CITED

- 1. D. P. Timofeev, Adsorption Rate [in Russian], Izd. Akad. Nauk SSSR, Moscow (1962).
- 2. P. P. Zolotarev and V. I. Ulin, Izv. Akad. Nauk SSSR, Ser. Khim., <u>1974</u>, 2829.
- 3. P. P. Zolotarev and V. V. Ugrozov, Izv. Akad. Nauk SSSR, Ser. Khim., 1981, 80.
- 4. I. A. Yabko and P. P. Zolotarev, Zh. Fiz. Khim., 54, 1807, 1813 (1980).
- 5. P. P. Zolotarev, P. P. Gladyshev, and V. Sh. Mamliev, Izv. Akad. Nauk SSSR, Ser. Khim., 1980, 2226, 2231.
- 6. A. M. Voloshchuk and M. M. Dubinin, Dokl. Akad. Nauk SSSR, 212, 649 (1973).
- A. V. Lykov, Theory of Heat Conductivity [in Russian], Vysshaya Shkola, Moscow (1967), p. 599.
- 8. P. P. Zolotarev, Teor. Osn. Khim. Tekhnol., 7, 603 (1973).

ADDITION OF NUCLEOPHILIC REAGENTS TO BIS(TRIFLUOROMETHYL) KETENE

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Nucleophilic reagents add easily to bis(trifluoromethyl) ketene (I) at the C=C multiple bond [1]:



At the same time, the reaction of (I) with HCN gives the enol acetate (II) [2], apparently by the addition of HCN to the C=O multiple bond and subsequent reaction of the intermediate enol (A) with a second molecule of (I):



An alternate variation of this scheme is the standard addition of HCN to the C=C bond of the ketene and the subsequent iosmerization of cyanide (B) to the enol form:

$$(I) \xrightarrow{HCN} \begin{bmatrix} O \\ \parallel \\ (CF_3)_2 CH \xrightarrow{\parallel} CN \xrightarrow{} (A) \end{bmatrix} \xrightarrow{(I)} (II)$$

A. N. Nesmeyanov Institute of Heteroorganic Compounds, Academy of Sciences of the USSR, Moscow. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 10, pp. 2408-2410, October, 1982. Original article submitted February 13, 1982. Compound (B) was not described, but there is reason to state that the enol is its thermodynamically more favorable form. This statement is based on the fact that enol form (C), which is an even weaker CH acid than acid (B), is thermodynamically stable [3]:



In view of the above-discussed result the addition of HCN to (I) cannot be regarded as a fact that testifies to the initial addition of a nucleophilic reagent to the C=O multiple bond.

We found that α -hydrohexafluorothiolisobutyric acid (III) reacts with excess (I) to give thioanhydride (IV) and enol acetate (V):



It was shown by **special experiment** that (I) does not react with thioanhydride (IV), which was found to be completely in the CH form (based on the NMR data).

The reaction of acid (III) with an equimolar amount of (I) at -78° C leads only to thioanhydride (IV). The pure enol acetate (V) was isolated by chlorinating a mixture of (IV) and (V) at 50°. Here (IV) is converted to easily removed low-boiling products, and specifically to hexafluoroisobutyryl chloride and SCl₂, while (V) remains unchanged.

Compounds (IV) and (V) were obtained by the reaction of (I) with H_2S . Acid (III), the intermediate formed in the given case, undergoes the above-described transformations:

 $(I) \xrightarrow{H_{2}S} [(III) \xrightarrow{(I)} [D]] \xrightarrow{(I)} (IV) + (V)$

The obtained results testify to the fact that thiol acid (III), and apparently other nucleophiles, add to (I) at the C=O bond.* As a rule, the enol forms that are formed here as intermediates are easily isomerized to the carbonyl forms, which in the final analysis add with equal vigor to the C=C multiple bond. The presence of stabilizing groups in the enol intermediates raises their stability and makes the rates of isomerization and addition to ketene (I) comparable. The enol form of intermediate (D) is apparently stabilized by the hydrogen bond with the carbonyl group.

Thiol acid (III) was obtained by the addition of either benzyl or tert-butyl mercaptan to ketene (I) and subsequent heating of the adduct with fluosulfonic acid:^{\dagger}

$$(I) + RSH \rightarrow (CF_3)_2 CHCOSR \xrightarrow{HSO_4F} (CF_3)_2 CH - C$$

$$(III a, b) \xrightarrow{\circ_C} (III) SH$$

 $\mathbf{R} = \mathbf{PhCH}_2$ (a); $\mathbf{Me_3C}$ (b)

EXPERIMENTAL

The ¹⁹F (84.6 MHz) and ¹H (60 MHz) NMR spectra were obtained on Perkin-Elmer R-32 and Perkin-Elmer R-12 spectrometers from CF_3COOH and TMS as the external standards. The IR spectra were recorded on a UR-20 spectrophotometer. The purity of the compounds was checked by

^{*}The addition of nucleophiles to the C=N bond of fluorinated ketenimines was observed in [4]. [†]The previously known method for the synthesis of acid (III) was the addition of H_2O to the difficultly available bis(trifluoromethyl) thicketene [5].

GLC on an LKhM-8MD instrument (Model 3), using a column packed with 20% QF-I deposited on Chromaton.

Benzyl Ester of α -Hydrohexafluorothioisobutyric Acid (IIIa). Ketene (I) (44.5 g, 0.25 mole) was passed at ~20° into 27 g (0.22 mole) of benzyl mercaptan, containing 3 drops of Nmethylpyrrolidone. The excess (I) was removed in vacuo. Distillation gave 57.7 g (88%) of (IIIa), bp 80-82° (2 mm). Found: C 43.17; H 2.57; F 37.65; S 10.03%. C11H8F6SO. Calculated: C 43.69; H 2.65; F 37.71; S 10.06%. Infrared spectrum (v, cm⁻¹): 1685 (C=0). PMR spectrum (in CC1₄): 4.2 s (CH₂); 4.3 hept [(CF₃)₂CH], 7.2 s (Ph). ¹⁹F NMR spectrum (in CC1₄): $-14.5 d [(CF_3)_2CH], J_{CF_3-H} = 7.5 Hz.$

tert-Butyl Ester of α-Hydrohexafluorothiolisobutyric Acid (IIIb). The same as the preceding, from 35.5 g (0.2 mole) of (I) and 15 g (0.17 mole) of tert-butyl mercaptan we obtained 40.3 g (91%) of (IIIb), bp 66-67° (40 mm). Found: C 35.84; H 3.81; F 42.42; S 12.14%. $C_8H_{10}F_6SO.$ Calculated: C 35.82; H 3.73; F 42.54; S 11.93%. Infrared spectrum (v, cm⁻¹): 1695 (C=O). PMR spectrum: 1.4 s (Me), 4.0 hept [(CF₃)₂CH]. ¹⁹F NMR spectrum: -13.7 d $[(CF_3)_2CH], J_{CF_3-H} = 7.5 Hz.$

α-Hydrohexafluorothiolisobutyric Acid (III). In a quartz glass distillation apparatus were placed 4.0 g (0.015 mole) of (IIIb) and 2 ml of freshly distilled FSO3H. The mixture was heated with a flame and the product distilling up to 120° was collected. The product from two experiments was dried over MgSO4, then distilled. We obtained 2.6 g (40%) of (III), bp 99-102°, ¹⁹F NMR spectrum: -12.9 d [(CF₃)₂CH], J_{CF₃-H} = 7.5 Hz (cf. [4]).

Anhydride of α -Hydrohexafluorothiolisobutyric Acid (IV). To 1.5 g (0.008 mole) of (I) at -70° was added 1.8 g (0,008 mole) of (III). The temperature of the mixture was slowly raised to $\sim 20^\circ$ and kept at this temperature for 30 min. We obtained 2.4 g (73%) of practically pure (IV). The analytical sample was purified by sublimation, mp 103° (in a sealed capillary). Found: C 24.50; H 0.72; F 57.93; S 8.17%. $C_8H_2F_{12}SO_2$. Calculated: C 24.60; H 0.51; F 58.30; S 8.21%. Infrared spectrum (v, cm⁻¹): 1760 (C=0). PMR spectrum (in Et₂0): 4.8 hept; [(CF₃)₂CH]. ¹⁹F NMR spectrum (in Et₂0): -14.0 d [(CF₃)₂CH], J_{CF₃-H = 7.5 Hz.}

Reaction of (III) with Bis(trifluoromethyl) Ketene (I). To a solution of 4.5 g (0.025 mole) of (I) in 5 ml of abs. ether was added in drops a solution of 1.0 g (0.005 mole) of (III) in 3 ml of abs. ether. The mixture was kept for 1 h at $\sim 20^{\circ}$, and then the excess (I) and the solvent were vacuum-distilled. The residue contained 2.1 g of a mixture that analyzed (GLC) 40% of (IV) and 60% of (V). The pure (V) was obtained from the indicated mixture by heating with 3 ml of Cl₂ in a glass ampul for 10 h at 50°. The excess chlorine and low-boiling products were vacuum-distilled. The residue contained 1.1 g of 1-bis(trifluoromethyl)thioacetoxy-l-bis(trifluoromethyl)acetoxyperfluoro-2-methyl-l-propene (V), mp 77° (in a sealed capillary). Found: C 25.35; H 0.35; F 60.21; S 5.63%. C₁₂F₁₈H₂SO₃. Calculated: C 25.40; H 0.41; F 59.85; S 5.71%. Infrared spectrum: (v, cm⁻¹): 1650 (C=C), 1730, 1790 (C=O). PMR spectrum (in Et_20): 4.78 hept [(CF₃)₂CH], 4.84 hept [(CF₃)₂CH], ¹⁹F NMR spectrum (in Et_20); -13.1 d [(CF₃)₂CH], -13.8 d [(CF₃)₂CH], -16.8 q (CF₃), -17.2 q (CF₃); $J_{CF_3-H} = 7.5$, $J_{CF_3-CF_3} = 7.5$ 9.4 Hz.

Reaction of Ketene (I) with H_2S . An excess of dry H_2S was passed for 1 h into a solution of 15.0 g (0.08 mole) of (I) in 40 ml of abs. ether. The gases and solvent were vacuumdistilled at 80°. The solid residue (17.1 g) was a mixture of 40% of (IV) and 60% of (V) (GLC).

CONCLUSIONS

When α -hydrohexafluorothiolisobutyric acid is reacted with bis(trifluoromethyl) ketene, the initial act is addition to the C=O multiple bond of the latter.

LITERATURE CITED

- 1.
- Y. A. Cheburkov and I. L. Knunyants, Fluor. Chem. Rev., <u>1</u>, 107 (1967). L. A. Símonyan, Z. V. Safronova, N. P. Gambaryan, M. Yu. Antipin, and Yu. T. Struchkov, 2. Izv. Akad. Nauk SSSR, Ser. Khim., 1980, 358.
- З. M. G. Voronkov, N. A. Keiko, T. A. Kuznetsova, V. A. Pestunovich, and I. D. Kalikhman, Dokl. Akad. Nauk SSSR, 247, 110 (1979).
- E. G. Ter-Gabrielyan, E. P. Lur'e, Yu. V. Zeifman, and N. P. Gambaryan, Izv. Akad. Nauk 4. SSSR, Ser. Khim., 1380 (1975).
- M. S. Raasch, J. Org. Chem., <u>37</u>, 1347 (1972). 5.