

ratios of the reactants were also chosen in the experiments with $(\text{PhCO})_2$ when generating the $\text{PhC(O)C(Ph)OSiEt}_3$ radicals. The concentrations of RCl and $(\text{PhCO})_2$ in the competing reactions are given in Table 2. As the standard for calculating the concentrations of the radicals we selected $[2,2,6,6\text{-Me}_4\text{-4-(PhCO)}_2\text{-C}_6\text{H}_2\text{NO}]_0 = 3 \cdot 10^{-3}$ mole/liter.

CONCLUSIONS

The rate constants for the addition of triethylsilyl radicals to α -phenyl-N-tert-butyl-nitrone ($k_{\text{add}} = (11 \pm 5) \cdot 10^6$ liter/mole \cdot sec) and 2,4,6-tri-tert-butyl-nitrosobenzene ($k_{\text{add}} = (1.5 \pm 0.3) \cdot 10^9$ liter/mole \cdot sec) at $\sim 20^\circ\text{C}$ were determined by the EPR method.

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IONIC HYDROGENATION IN THE PRESENCE OF SURFACE-ACTIVE SUBSTANCES

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The rate of many chemical reactions depends on the presence of surface-active substances (SAS) in the reaction medium [1]. Frequently this is related to the formation of micelles, and in this case the accelerating effect of the SAS is called micellar catalysis. The vast majority of the data on micellar catalysis was obtained for aqueous solutions. Data on micellar catalysis in organic solvents is very scanty, although it is specifically such reactions that have interest for synthetic organic chemistry.

We studied the possible catalytic effect of the SAS in the ionic hydrogenation reaction [2]. The key step of this reaction is the formation of the carbocation, and consequently we used SAS which form micelles that are capable of stabilizing the intermediate carbenium ion, and specifically the Na salt of the diisooctyl ester of sulfosuccinic acid (I), poly(ethylene glycol 12-monolaurate) (II), and poly(ethylene glycol 10-oleate) (III). The substrates were olefins of variable structure and acetophenone, as the proton donor we used 68% HClO_4 ,[†] the triethyl- and diphenylsilanes served as the hydride-ion donors, and the solvent was n-octane, in which (I)-(III) form micellar solutions [4]. It proved that all of the studied SAS substantially accelerate the ionic hydrogenation of branched olefins and acetophenone (Table 1).

From Table 1 it can be seen that the ionic hydrogenation rules, established using the standard silane: CF_3COOH system, are retained, and unbranched olefins, in particular cyclohexene, are not hydrogenated, while acetophenone is reduced to the hydrocarbon.

*Deceased.

[†]The use of HClO_4 as the proton donor in ionic hydrogenation was shown in [3].

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TABLE 1. Ionic Hydrogenation in the Presence of SAS
(0.5 mmole of substrate; substrate:HClO₄:silane =
1:3:1.5 (molar); 1 ml of 0.1 M SAS solution in octane;
20°C; 1 h)

Substrate	SAS	Hydrogenation product	Yield, %
1-Methylcyclohexene	—	Methylcyclohexane	6
»	(I)	»	40
»	(II)	»	61
»	(III)	»	69
2,3-Dimethyl-2-butene	—	2,3-Dimethylbutane	4
»	(I)	»	41
»	(II)	»	65
»	(III)	»	68
2-Methyl-2-decene	—	2-Methyldecane	2
»	(I)	»	47
»	(II)	»	63
»	(III)	»	79
Acetophenone	—	Ethylbenzene	1
»	(II)	»	69
»	(III)	»	72
Cyclohexene	—	Cyclohexane	0
»	(I) - (III)	»	0

The studied SAS lead to high yields of the hydrogenation products at concentrations of 0.1-0.5 M, whereas the recently described carriers of the acid from the aqueous layer to the organic layer, and specifically alcohols and ethers with long alkyl chains, efficiently accelerate the ionic hydrogenation of the same substrates only at concentrations on the order of 1 M [3].

EXPERIMENTAL

All of the substrates and n-octane were purified by distillation, the 68% HClO₄ solution was prepared by evaporating the commercial acid in an argon stream below 150°C, and the SAS were used as such.

The reactions were run by the following general method. To 1 ml of the SAS solution in n-octane of known concentrations were added a mixture of 0.5 mmole of the substrate with the standard (for the GLC analysis) and the organohydrosilane and then the calculated amount of 68% HClO₄ solution (see Table 1). The mixture was stirred at 20°C for 1 h, and the organic layer was separated and neutralized with soda. The reaction products were analyzed by GLC on Chrom-3 and Chrom-41 instruments, using 10% of PEGA deposited on Risorb BLK and 5% of Apiezon deposited on Chromosorb G. The yields of methylhexane, 2,3-dimethylbutane, 2-methyldecane, ethylbenzene, and cyclohexane were determined with n-heptane, cyclohexane, n-dodecane, o-xylene, and n-hexane as the internal standards respectively.

CONCLUSIONS

Surface-active substances can be efficient catalysts of the ionic hydrogenation reaction.

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