ISSN 1070-4272, *Russian Journal of Applied Chemistry, 2007, Vol. 80, No. 9, pp. 1566–1569. © Pleiades Publishing, Ltd., 2007.*
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## ORGANIC SYNTHESIS AND INDUSTRIAL ORGANIC CHEMISTRY

# In Situ Version of Radical-Chain Substitution Reactions

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Received April 27, 2007

**Abstract**—Peroxy acetals derived from an ether and a hydroperoxide can be prepared in situ and used without isolation to effect sulfochlorination of *n*-alkanes or chlorination of toluene to benzyl chloride.

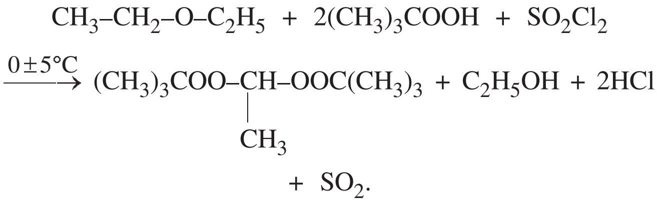
**DOI:** 10.1134/S1070427207090236

The feasibility of initiated radical processes using activators prepared in situ in the reaction volume is obvious. The interest in such way of initiating chain reactions is particularly pronounced in production of polymers, e.g., of suspension PVC [1]. Acyl peroxides prepared in a polymerizer from a hydrogen peroxide salt and an acyl chloride in the monomer–water system are fairly effective. Peroxydicarbonates and sulfonyl peroxides are also used.

Common liquid-phase radical-chain reactions involving C–H substitution, such as chlorination and sulfochlorination of hydrocarbons, are performed in the bulk of a hydrocarbon or in a nonpolar solvent. The components of the chemical initiating system should be readily soluble or uniformly distributed in the hydrocarbon (RH). The majority of organic peroxides described in the literature are used in both polymerization and substitution reactions [2]. However, there are virtually no data in the literature on the use of a reaction mixture of initiator synthesis (without its isolation) for initiating a chain substitution reaction. In a sulfochlorinator or a chlorinator, the presence of oxygen and water, which are frequently used components in syntheses of peroxides, is inadmissible.

Here we consider a version of initiator synthesis in situ in the reaction volume, followed by an initiated substitution reaction. As investigation objects we chose well-known aldehyde derivatives, peroxy acetals.

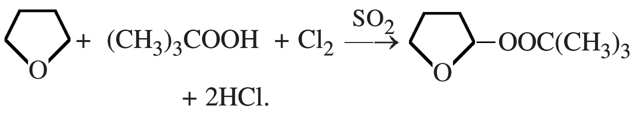
Of particular practical value is the procedure for preparing mono- and diperoxy acetals from ethers and hydroperoxides in the presence of sulfuryl chloride $SO_2Cl_2$ or evaporated $Cl_2$ (taken separately or in a mixture with $SO_2$), described in [3]. It was demonstrated by numerous examples that aliphatic and cyclic (unstrained) ethers can be vigorously oxidized with *tert*-butyl hydroperoxide (TBHP) at the α-H atom relative to the ether bond. For example, 1,1-di-*tert*-butylperoxyethane (DTBPE) is rapidly formed in a good yield at the molar ratio $Et_2O$ : TBHP : $SO_2Cl_2$ = (10–5) : (3–2.3) : 1 by the reaction



$$CH_3\text{–}CH_2\text{–}O\text{–}C_2H_5 + 2(CH_3)_3COOH + SO_2Cl_2 \xrightarrow{0\pm5°C} (CH_3)_3COO\text{–}\underset{\displaystyle CH_3}{\underset{|}{CH}}\text{–}OOC(CH_3)_3 + C_2H_5OH + 2HCl + SO_2.$$

There is certain evidence that the reaction occurs via formation of the monoperoxy acetal, 1-ethoxy-1-*tert*-butylperoxyethane.

High yield was attained with a 1 : (1–0.2) mixture of $Cl_2$ and $SO_2$ taken instead of $SO_2Cl_2$. For example, 2-*tert*-butylperoxytetrahydrofuran (TBPTHF) is prepared in >90% yield on the standard equipment of chlorine plants [3] by passing $Cl_2$ and $SO_2$ evaporated from cylinders through a solution of TBHP in THF at 5–10°C for 20 min:



The procedure of synthesis of peroxy acetals fortunately matches the substitution reactions with respect to reagents, equipment, temperature, and reaction rate, which opens real prospects for simplifying the step of chemical initiation of chlorination and sulfochlorination of hydrocarbons. Indeed, under the conditions typical for the formation of an alkanesulfonyl chloride from a liquid alkane and a mixture of $SO_2$ and $Cl_2$ at 30–35°C,

$$R\text{–}H + SO_2 + Cl_2 \rightarrow RSO_2Cl + HCl,$$

it is absolutely unnecessary to prepare an initiator (e.g., TBPTHF, an effective sulfochlorination initiator [4]) in a separate step.

Before feeding the gases, it is sufficient to add a solution of TBHP in THF to the hydrocarbon and make sure that the initiator has formed in situ in the sulfochlorinator and affected the parameters of the reaction mixture.

The most important reaction parameter is the rate of accumulation of hydrolyzable chlorine $Cl_h$ after Volhard. The figure shows the results of experiments under similar conditions with TBPTHF prepared beforehand (curve *3*) and in situ (curve *4*), and also with TBHP (curve *2*). These data show that the degree of sulfochlorination, and also the conversion of $Cl_2$ and RH (evaluated by various procedures) are higher when the initiator is prepared in situ, compared to the separate preparation of the initiator or UV initiation [4].

The idea put forward [4] was indirectly supported by experiments on revealing effective chemical initiators of toluene chlorination with sulfuryl chloride:

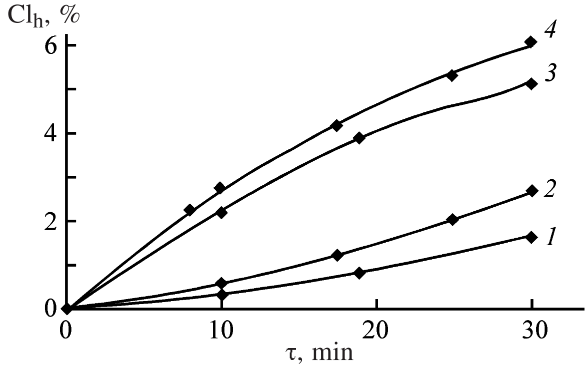
$$C_6H_5CH_3 + SO_2Cl_2 \longrightarrow C_6H_5CH_2Cl + SO_2 + HCl.$$

Benzyl chloride is obtained in a high yield only in the presence of benzoyl and lauryl peroxides and AIBN in amounts of 0.001–0.005 mol per mole of toluene, including experiments with 1 : 1 reactant ratio and heating for 20–30 min [5]. Without initiators, toluene does not react with $SO_2Cl_2$ even under refluxing for 6 h. In many books, this transformation is considered as a particular reaction: The reaction is selective owing to formation of the $^\bullet SO_2Cl$ radical in the initiation [2] and chain propagation steps. The reaction

$$Inc^\bullet + SO_2Cl_2 \longrightarrow IncCl + {}^\bullet SO_2Cl$$

is probable owing to fragmentation of the initially formed acyloxy radicals $R''COO^\bullet$ to $R''^\bullet$, followed by the reaction of $R''^\bullet$ with the reagent.

The results of experiments on preparation of benzyl chloride showed that in situ synthesis of peroxy acetals in the chlorinator ensures higher yield of the final product compared to the synthesis with the ready initiator (52±2°C, 30 min; see table). For comparison we used a protocol of the synthesis of benzyl chloride by the reaction of RH with $SO_2Cl_2$ at the molar ratio of the reactants of 1 : 0.5 in the presence of AIBN [5].



Accumulation of $Cl_h$ with time τ in a dark vessel. (*1*) No initiator, (*2*) ~0.005 M TBHP, (*3*) ~0.005 M TBPTHF, and (*4*) 0.07 g of TBHP (72%) in 1.2 ml of THF (~0.005 M peroxide in reaction mixture). Gas supply rate 0.3 g $min^{-1}$ each. RH weight, g: (*1*, *3*) 73 and (*2*, *4*) 72.

Under these conditions (run no. 1), the reaction is essentially incomplete. By distillation under reduced pressure, we isolated from the reaction mixture, along with benzyl chloride, also the unchanged reactants: toluene (63.4%) and $SO_2Cl_2$ (23.8%). Despite considerable differences in the boiling points of the mixture components, pure benzyl chloride cannot be isolated by single distillation; repeated distillation, desirably with a dephlegmator, is required.

When the peroxy acetal is prepared in the chlorinator in situ (run nos. 4–6), 98.7% pure (GLC data) benzyl chloride can be readily isolated by single distillation (run no. 4).

In the suggested procedure for preparing benzyl chloride [6], it is possible to attain almost quantitative conversion of the reactants with 85–90% product yield. The order of mixing the components exerts a noticeable influence. When a solution of TBHP in an ether is added to toluene before adding $SO_2Cl_2$, the

Yield of benzyl chloride with various initiators

| Run no. | Initiator | | | Yield, % |
|---|---|---|---|---|
| | name | amount | | |
| | | g | mmol* × $10^3$ | |
| 1 | AIBN, mp 103°C | 0.200 | 1.23 | 68.8 |
| 2 | 92% TBHP | 0.118 | 1.25 | Traces |
| 3 | 96% TBPTHF | 0.387 | 2.35 | 50.4 |
| 4 | TBPTHF, in situ** | 0.122 | 1.10 | 71.5 |
| 5 | The same, from 92% TBHP | 0.343 | 4.36 | 88.2 |
| 6 | The same, from 92% TBHP | 0.398 | 5.06 | 77.8 |

* Per mole toluene. Toluene amount: 92 g in run nos. 1–4, 74 g in run nos. 5 and 6.

** From 85% TBHP.

product yield is always 5–10% higher than when a solution of TBHP in an ether is added to the reactant mixture (run no. 6, as in run no. 1).

Thus, the mechanism of the effect of peroxides prepared in situ in the reaction vessel should not differ from the mechanism of the effect of pure peroxides (as sources of alkoxy radicals) on the system with predominance of RH:

$$0.5\text{R''OOR''} + \text{RH} \longrightarrow \text{R''OH} + \text{R}^{\bullet}.$$

The dissociation of the O–O bond in mono- or diperoxy acetals should not be considered separately from the escape ot the resulting radicals into the bulk of solution. It is improbable, e.g., that the *tert*-butoxy radical would react with a chlorinating agent (including $SO_2Cl_2$) in the presence of RH (irrespective of whether RH is toluene or *n*-alkane).

The procedure suggested in [6] for preparing benzyl chloride is also very selective (the content of benzal chloride is as low as 0.25%), compared to chlorination of toluene with elemental $Cl_2$ in the presence of known initiators [2]. Presumably, the considerable differences between the results obtained with different chlorinating agents ($Cl_2$ or $SO_2Cl_2$) are associated with the structure and energy of the transition state in the chain propagation step involving these agents, at least provided that the benzyl radical $C_6H_5CH_2^{\bullet}$ is formed in the chain initiation step under the action of peroxides as generators of alkoxy radicals.

The initial component of the initiating system we suggest is TBHP, one of the most readily available organic peroxides whose commercial production is well mastered. At 30–50°C, the O–O bond in TBHP in hydrocarbon solutions does not noticeably dissociate. Experiments (figure, curve *2*; table, run no. 2) show that straight TBHP, irrespective of purity (chemically pure or technical grade), shows no promise for intensification of radical substitution reactions. The hydroxy derivative may react with $SO_2Cl_2$ as acid chloride or be reduced with $SO_2$. The latter process (at a high $SO_2Cl_2$ concentration) is, apparently, responsible for the low yield of the product when the chlorination is performed in the presence of TBPTHF (table, run no. 3) or when the initiating system is added to the reactants mixed beforehand (run no. 6).

Activation of the hydroperoxide with an ether or, more precisely, use of a mixture of TBHP with an ether for in situ preparation of a peroxy acetal (without its isolation) in the reaction volume is a simple way of effective initiation of substitution reactions.

## EXPERIMENTAL

Freshly prepared peroxides with a high content of available oxygen ($O_a$; iodometric titration) were used. In all the cases the initiator was added into the hydrocarbon, after which the chlorinating agents were added. The initiator concentration is given counting on 100% purity.

Sulfochlorination of a liquid paraffin was performed in a round-bottomed vessel equipped with a bubbler for feeding gases, a stirrer, a reflux condenser, and a thermometer. The chlorinating mixture components, $SO_2$ and $Cl_2$, were evaporated from cylinders, dried, and fed in 1.1 : 1 ratio, using rheometers, to the reaction mixture at $30 \pm 2$°C. As alkane we used synthine, TU (Technical Specification) 602-953–77, used in production of ionic surfactants, alkanesulfonates.

Synthine (synthetic paraffin) is a mixture of $C_{12}$–$C_{18}$ *n*-alkanes with the mean molecular weight of 198; $d_4^{20}$ 0.764–0.768, flash point 85°C, bp $290 \pm 65$°C.

With TBPTHF prepared in situ from TBHP and THF in the sulfochlorinator, the reaction mixture parameters (figure, curve *4*) after blowing-off are as follows: $d_4^{20}$ 0.8627, $n_D^{20}$ 1.4458, $Cl_h$ 5.65%, weight gain 1.15 g per gram of RH. The conversion evaluated from $Cl_h$ is ~100% for $Cl_2$ and 34.89% for RH. In experiments described by curves *1–3*, the conversion and weight gain were lower.

### *Chlorination of Toluene with Sulfuryl Chloride in the Presence of Initiator Prepared in situ in the Chlorinator*

**Synthesis of benzyl chloride using TBPTHF prepared in situ from TBHP and THF** (table, run no. 5). A reactor equipped with a stirrer, a reflux condenser, and a thermometer was charged with 74.0 g (0.8 mol) of toluene [analytically pure grade, GOST (State Standard) 5789–78], after which a solution of 0.343 g of TBHP (92% pure according to iodometric titration data) in 1.8 ml of THF was added. This amount corresponds to 0.004359 mol of TBPTHF per mole of toluene. Then 54.0 g (0.4 mol) of $SO_2Cl_2$ (bp 69°C, $d_4^{20}$ 1.667) was added. The mixture warmed up to spontaneously to 37°C, and, before the temperature started to decrease, it was heated to $54 \pm 4$°C and kept at this temperature for 30 min. The resulting mixture (89.0 g) was distilled from a Claisen flask. The following fractions were obtained: unchanged toluene (46.7 g, bp 54–56°C/100 mm Hg, $n_D^{20}$ 1.4963, $d_4^{20}$ 0.864) and benzyl chloride (33.1 g, bp 92–93°C/

43 mm Hg, $n_D^{20}$ 1.5392, $d_4^{20}$ 1.102, in agreement with reference data). According to GLC, the benzyl chloride was 99.35% pure (which is similar to the purity of a commercial sample after fractional distillation [6]). The residue was a dark tar (1.4 g). The yield of benzyl chloride was 88.24% (based on converted toluene, without taking into account the residue).

**Synthesis of benzyl chloride with DTBPE prepared in situ from TBHP and diethyl ether.** A stirred reactor was charged in succession with 46.1 g (0.5 mol) of toluene, a solution of 0.22 g of 85% TBHP in 1.5 ml of diethyl ether (which corresponds to 0.00206 mol of DTBPE per mole of toluene), and 27.1 g (0.2 mol) of sulfuryl chloride. The mixture warmed up virtually immediately, and vigorous gas evolution started. Although at 52 ± 2°C visually observed gas evolution practically ceased 15 min after the start of the reaction, the reaction was performed for 30 min. By simple distillation of the mixture (55.3 g), 29.0 g (33.5 ml) of unchanged toluene (bp 60–62°C/96 mm Hg) was obtained. Further distillation gave 20.1 g of a product with $d_4^{20}$ 1.104, bp 71–74°C/17–18 mm Hg, $n_D^{15}$ 1.5411, which agrees with the reference data for pure benzyl chloride. Yield of benzyl chloride 85% based on converted toluene or 79.5% based on converted sulfuryl chloride. This is good agreement taking into account possible loss of low-boiling $SO_2Cl_2$.

## CONCLUSION

A mixture of *tert*-butyl hydroperoxide with an aliphatic or cyclic ether was suggested for in situ generation of peroxy acetals in a chlorinator or a sulfochlorinator with the aim of effective initiation of radical-chain C–H substitution reactions in hydrocarbons.

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