

On the Ritter Synthesis of N-tert-Butylacrylamide (Part II)* Reaction between tert-Butylalcohol and Acrylonitrile in Non-aqueous Solvents

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ABSTRACT

The Ritter reaction between tert-butylalcohol and acrylonitrile with sulfuric acid as catalyst in excess anhydrous acetic acid or acrylonitrile is investigated. A somewhat different course of reaction as with isobutylene was found. High yields of N-tert-butylacrylamide with 80-98 % sulfuric acid at mild temperatures could be obtained but a partial sulfonation of the amide with concentrated or fuming sulfuric acid at higher temperatures was established. A kinetic study of the amide formation is carried out.

Key Words

synthesis, conversion, yield, acid-catalysis, kinetics

INTRODUCTION

N-tert-butylacrylamide (TBAA) is a monomer of significant interest in polymer chemistry [1]. In the general and patent literature there are examples of the preparation of this monomer by the sulfuric acid catalyzed reaction of either isobutylene or tert-butylalcohol (t-BuOH) with acrylonitrile [2-7]. Except for the early work of Glikmans and his co-workers who, at that time, reported an unrealistic mechanism of TBAA formation in excess anhydrous acetic acid [7,8], neither was a comparative study between the reactivity of the olefin and tertiary alcohol carried out nor was the particular effect of sulfuric acid on the course of this reaction studied in any detail.

In a recent paper, a re-examination of the reaction system isobutylene-acrylonitrile-sulfuric acid in excess anhydrous acetic acid or acrylonitrile has been reported [9]. It has been found that irrespective of the reaction conditions used, a mixture of variable ratios of TBAA and the water-soluble monomer 2-acrylamido-2-methylpropanesulfonic acid (AMPS) is always obtained. Both monomers are simultaneous products of typical Ritter synthesis.

The present paper is concerned with some new contributions on the sulfuric acid catalyzed reaction of t-BuOH and acrylonitrile, in the same solvent media, to look for the possibility of a

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selective synthesis of TBAA which may be useful for technological aims.

EXPERIMENTAL

Materials

Freshly distilled acrylonitrile (ACN), reagent grade t-BuOH, TBAA, concentrated and fuming sulfuric acid were used without further purification. Different concentrations of sulfuric acid in the range of 80-98 wt % and of fuming sulfuric acid of up to 20 wt % free of SO₃(SA) were prepared by appropriate adjustments of concentration. Anhydrous acetic acid (AcOH) was prepared by anhydritization with acetic anhydride.

Methods

A time-dependent study of TBAA and AMPS formation, if any, was obtained by a combination of gravimetry, UV-spectrophotometry and analytical techniques. The dissolved TBAA, AMPS and sulfuric acid in the reaction mixture were evaluated by the same procedures described previously [9]. Equimolar amounts of t-BuOH and ACN were used for reaction in excess anhydrous acetic acid. A 9-fold molar excess of solvent (AcOH, ACN) and concentrations of t-BuOH and sulfuric acid ranging from 0.10 to 2.0 mol.L⁻¹ were investigated. The proper conditions experimentally found for the preparation of TBAA as a single reaction product were selected for kinetic measurements. To monitor the progress of the reaction, aliquots were removed at regular intervals, poured in alkaline water - methanol mixtures (8 : 2 by vol) to cease the reaction and after corresponding diluting with distilled water, subjected to quantitative UV-analysis. The absorbance maxima (A) were recorded and the increasing amounts of TBAA were calculated from the calibration curve (SPECORD M-42 Carl Zeiss, at 225 nm, ε_{max} = 6000 mol⁻¹.L.cm⁻¹). The standard kinetic equations for calculation of first and second-order rate constants were used:

$$k_1 = \frac{\epsilon}{t} \ln \frac{A_\infty}{A_\infty - A_t} \text{ and } k_2 = \frac{\epsilon}{t} \left[\frac{1}{A_\infty - A_t} - \frac{1}{A_\infty} \right]$$

RESULTS AND DISCUSSION

As has been already shown for the reaction of isobutylene with acrylonitrile, in excess anhydrous acetic acid, TBAA is the preferred reaction product while using sulfuric acid of less than 98 wt % concentration [9]. An increased content of AMPS, even exceeding that of TBAA, was generally observed on increasing temperature and concentration of the sulfuric acid used. For example, quite comparable yield values of TBAA and AMPS were obtained at 20-30 °C with equimolar amounts of isobutylene, acrylonitrile and 98 wt % sulfuric acid. At the same time, in excess acrylonitrile, the prevalent formation of AMPS at considerably lower temperatures and concentrations of sulfuric acid was established. It has been also found that AMPS is obtained in a two-step reaction process due to the in-situ splitting up of the sulfuric acid molecule which delivers both SO₃ for a partial sulfonation of isobutylene and water for the subsequent acid catalyzed condensation of the sulfonated intermediate with acrylonitrile. This process occurs predominantly in an excess of acrylonitrile.

The t-BuOH may be thought as a hypothetical monohydrate derivative of isobutylene. That is, the stoichiometric amount of water for the Ritter synthesis of TBAA is always available even in anhydrous reaction media because of the chemically bound water in the t-BuOH molecule. Therefore, appreciable differences between isobutylene and t-BuOH for the same experimental conditions are to be expected.

As is evident from the data in Figure 1, the yield of TBAA increases almost linearly with the amount of sulfuric acid added, in an excess of both solvents. With equimolar amounts of 98 wt % sulfuric acid and t-BuOH (1.0 - 2.0 mol.L⁻¹) practically quantitative conversions to TBAA, at 20-30 °C, are easily achieved in a couple of hours.

A considerable increase of the reaction rate, as presented by the percent conversion of TBAA, on increasing the content of sulfuric acid in the mixture is also established. Some kinetic graphs for

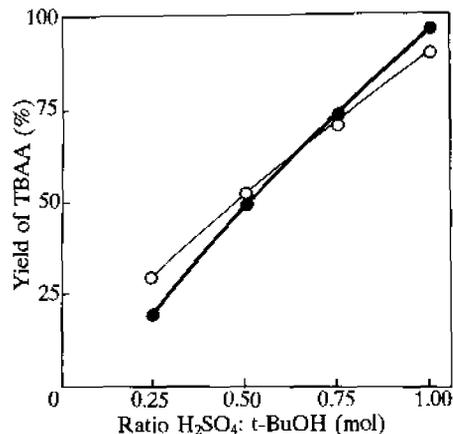


Fig. 1. Effect of the ratio of sulfuric acid on the yield to TBAA c_{t-BuOH} , mol.L⁻¹: 1.0; SA = 98 wt % H₂SO₄.

◆ In ACN, 20 °C, 5hr.
○ In ACN, 30 °C, 5hr.

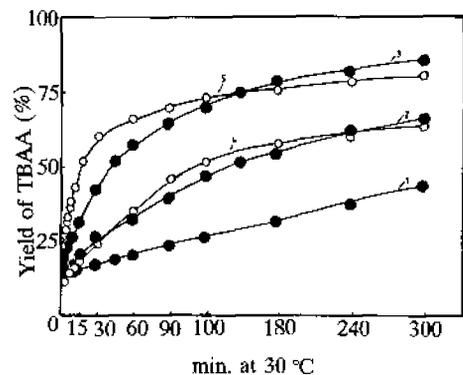


Fig. 2. Time-conversion relationships at various concentrations of sulfuric acid, in excess AcOH.

c_{t-BuOH} , mol.L⁻¹: 0.20 (◆); 1.50 (◇).
 $c_{H_2SO_4}$, mol.L⁻¹: 0.10 (1), 0.20 (2), 0.40 (3), 0.75 (4), 1.125 (5).

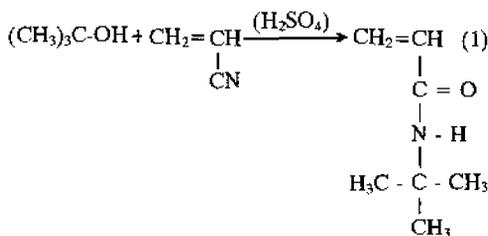
the reaction carried out in anhydrous acetic acid are illustrated in Figure 2. For fixed temperature

and concentration of sulfuric acid, the TBAA percentage increased regularly up to 50-60 % conversion but the reaction then slowed considerably. This may be likely explained because of a TBAA-H₂SO₄ reversible adduct formation which apparently causes a decrease of the "free" sulfuric acid in the system as the reaction proceeds. Such associations in binary systems of the amide-acid type by intermolecular hydrogen bonding are generally ascertained [10,11].

Some experimental data concerning the influence of temperature as well as the nature of the solvent (diluent) on the course of reaction, in practically anhydrous conditions, are summarized in Table 1.

Unlike isobutylene, quite similar results are obtained with t-BuOH in anhydrous acetic acid or acrylonitrile. The very differentiating role of the solvent pointed out previously in the reaction with isobutylene [9] becomes now of very little importance. Thus, in a range of temperature range of 15-50 °C, the formation of TBAA appears to be the only path of reaction in the system t-BuOH-acrylonitrile-sulfuric acid of 80-98 wt % concentration, in an excess of both selected solvents. No AMPS could be made evident until about 60 °C.

Consequently, only the catalytic effect of the sulfuric acid has to be considered with t-BuOH in such conditions (equation 1).



The reaction between t-BuOH and acrylonitrile in the presence of concentrated sulfuric acid, as monitored spectroscopically, followed second-order kinetics with respect to the reactant concentrations up to about 50 mol % conversion to TBAA. Until the same extent of

Table 1. Effect of temperature and the nature of the solvent on the distribution of the reaction products.

Solvent (Diluent)	Temperature (°C)	Reaction Products		Apparent rate constants	
		TBAA (mol %)	AMPS (mol %)	$10^3 k_1^{exp}$ (min ⁻¹)	$10^3 k_2^{exp}$ (mol ⁻¹ .L.min ⁻¹)
AcOH	60	81	≤3.0	-	-
AcOH	50	75	-	-	88.60
AcOH	40	64	-	-	37.91
AcOH	30	53	-	-	16.97
ACN	60	80	≤3.0	-	-
ACN	50	77	-	119.7	139.7
ACN	40	69	-	60.16	73.4
ACN	30	56	-	30.2	37.4
ACN	20	49.4	-	15.50	20.0

$c_{(t-BuOH, ACN)}$: 1.50 mol.L⁻¹; $c_{H_2SO_4}$: 0.75 mol.L⁻¹; SA: 98 wt - % H₂SO₄; 10 hr.

Activation energies: in ACN, 12.20 Kcal.mol⁻¹ (from k_2^{exp}); 12.90 Kcal.mol⁻¹ (from k_1^{exp}) in AcOH, 16.10 Kcal.mol⁻¹.

conversion, the scheme of pseudo-first-order kinetics may also be used to evaluate the rate constants in a great excess of acrylonitrile. For comparison, the apparent rate-constants (k^{exp}), determined at different temperatures but at constant concentration of sulfuric acid, are reported in Table 1.

The reaction rate is also proportional to the Hammett H_a function, in accordance with previous observations for acid catalyzed reactions [8, 12, 13]. Hence, the reaction is described by the kinetic equation (2)

$$v = dc_{TBAA}/dt = k_2^{exp} \cdot c_{ACN} \cdot c_{t-BuOH} \quad (2)$$

with $k_2^{exp} = k_2 \cdot h_a^\alpha$ and $H_a = -\log h$.

A linear relationship was found for $\log k_2^{exp}$ versus concentration of the sulfuric acid used or the Hammett acidity function H_a, respectively. Taking the reported scale values of H_a for the sulfuric acid-acetic acid mixtures at 25 °C [14], within the range of concentrations under investigation, the following values of α (30 °C) were obtained:

$$c_{(t-BuOH, ACN)}, \text{ mol.L}^{-1}: 0.10 - 0.20 \quad 1.40 - 1.60$$

$$c_{H_2SO_4}, \text{ mol.L}^{-1}: 0.10 - 0.40 \quad 0.40 - 1.60$$

$$\alpha: \quad 0.84 \quad 1.40$$

Assuming that the acidity function H_a is temperature - independent [14,15] the corresponding values of k_2 and v can be evaluated. Some data are reported in Table 2.

As shown in Tables 1 and 2 the reaction rate is slightly higher in acrylonitrile and usually increased with increasing concentration of the reaction components.

The concentration of the sulfuric acid used can affect considerably the course of reaction between t-BuOH and acrylonitrile especially at higher values of temperature. Thus, the formation of AMPS becomes evident and significantly increased upon increasing the temperature and/or by using fuming sulfuric acid (Table 3).

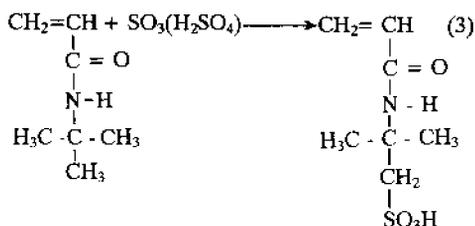
A partial sulfonation of t-BuOH through the intermediate dehydration to isobutylene is very improbable in such reaction conditions [16-18] and more likely appears to be the direct sulfonation of the TBAA already produced in the system (equation 3).

From the data in Table 3 it is obvious that increased yields of AMPS with simultaneous decrease of TBAA at higher concentrations of the acid are obtained, in good agreement with the

Table 2. Variation of rate constants with sulfuric acid concentration for the formation of TBAA in AcOH, 30 °C.

$c_{(t\text{-BuOH, ACN})}$ (mol.L ⁻¹)	$c_{\text{H}_2\text{SO}_4}$ (mol.L ⁻¹)	- H ₀	10 ³ k ₂ ^{exp} (mol ⁻¹ .L.min ⁻¹)	k ₂ (mean value) (mol ⁻¹ .L.min ⁻¹)	10 ³ v (mol ⁻² .L ² .min ⁻¹)
1.50	0.375	2.43	4.4		10.05
1.50	0.750	2.88	17.0		38.74
1.50	1.125	3.20	58.2	5.97 10 ⁻³	139.50
1.50	1.500	3.42	101.4		216.16
0.20	0.10	1.70	70.3		2.67
0.20	0.15	1.92	106.0		3.96
0.20	0.20	2.08	135.0	3.94 10 ⁻²	5.20
0.20	0.30	2.29	208.0		7.77
0.20	0.40	2.47	276.0		9.86

Activation energy ($c_{(t\text{-BuOH, ACN, H}_2\text{SO}_4)} = 0.20 \text{ mol.L}^{-1}$, 20-50 °C): 7.665 Kcal.mol⁻¹



unreacted sulfuric acid, H₂SO₄^(ur), determined in the reaction mixture. In all experiments no precipitation of AMPS occurred due to its solubility in the high fractions of the unreacted sulfuric acid.

The assumption of a partial sulfonation of TBAA was experimentally checked by a time-dependent study of the composition of the reaction mixture. The amounts of TBAA, AMPS and H₂SO₄^(ur) at appointed time intervals were simultaneously evaluated (Figures 3 and 4). Under the action of fuming sulfuric acid of 18 wt % free SO₃, a considerable conversion extent of TBAA to AMPS by sulfonation could be detected. About 38 mol % of the TBAA initially produced even in the mixing step of the reagents, at 25-30 °C, is converted to AMPS after about 20 hours, at 80 °C in acetic acid. At the same time, only a slight

variation versus time of the content of AMPS, up to 12 mol %, was measured at 30 °C (Figure 3). A similar variation of the system composition with time for the reaction in excess acrylonitrile, but in a lesser degree of TBAA conversion to AMPS, at

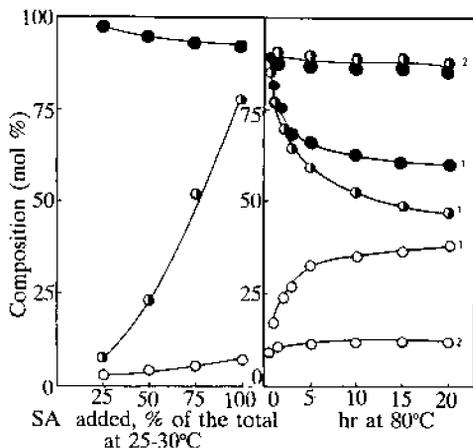


Fig.3. Reaction between t-BuOH and ACN in excess AcOH.

$c_{t\text{-BuOH}}$: 1.50 mol.L⁻¹
 Ratio t-BuOH: ACN: SA = 1.0:1.0:1.0 (mol)
 SA: fuming sulfuric acid of 18 wt % SO₃
 ○- AMPS; ●- TBAA; ■- H₂SO₄^(ur)
 80 °C (1); 30 °C (2).

Table 3. Effect of sulfuric acid (SA) concentration on the distribution of the reaction products.

Solvent (Diluent)	SA (wt %)	Ratio SA: t-BuOH (mole)	Reaction Products		H ₂ SO ₄ ^(<i>un</i>) (%)
			TBAA (mol %)	AMPS (mol %)	
AcOH	with 18 % SO ₃	1.0:1.0	47.5	38.8	61
AcOH	98	1.0:1.0	50.9	34.1	66
AcOH	93	1.0:1.0	61.6	26.2	72
AcOH	88	1.0:1.0	65.0	22.0	78
AcOH	85	0.5:1.0	62.0	8.0	86
ACN	with 18 % SO ₃	1.0:1.0	88.2	10.5	89
ACN	with 4 % SO ₃	1.0:1.0	90.1	6.0	93

c_{t-BuOH}: 1.46-1.50 mol.L⁻¹

Temperature: 80 °C (AcOH), 60 °C (ACN).

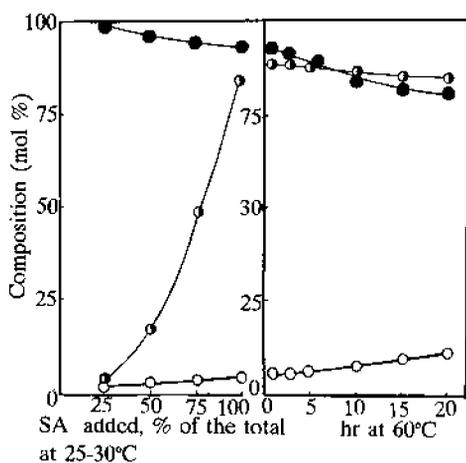


Fig.4. Reaction between t-BuOH and ACN in excess ACN.

c_{t-BuOH}: 1.50 mol.L⁻¹

Ratio t-BuOH: SA = 1.0:1.0 (mol)

SA: fuming sulfuric acid of 18 wt % SO₃

○, ●, ● Symbols as in Figure 3.

60 °C, was also found (Figure 4).

Attempts were also made in order to establish the action of fuming sulfuric acid on TBAA in similar reaction conditions. Such an experiment, under the same conditions used for

the plot in Figure 3, but starting with TBAA instead of t-BuOH, is illustrated in Figure 5. After 20 hours, at 80 °C, in excess anhydrous acetic acid, an equilibrium was achieved and a composition of almost 53 mol % unreacted TBAA and 35 mol % AMPS in the reaction mixture was evaluated. A corresponding decrease of the initial quantity of the sulfuric acid was also established.

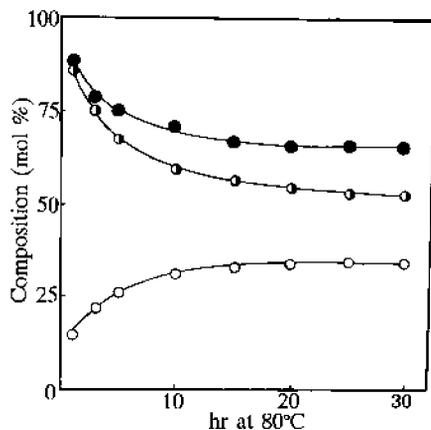


Fig.5. Reaction between TBAA and fuming sulfuric acid of 18 wt % SO₃, 80 °C, in excess AcOH.

c_{TBAA}: 1.50 mol.L⁻¹

Ratio TBAA: SA: AcOH = 1.0:1.0:9.0 (mol)

○, ●, ● Symbols as in Figures 3, 4.

Only very small degrees of conversion of TBAA to AMPS in the same reaction at room temperature were obtained. For example, after 24, 72 and 840 hours, only 2.0, 4.0 and 12.0 mol %, respectively, of the initial TBAA were converted to AMPS.

A somewhat similar fact was early mentioned in the acid-catalyzed formation of TBAA from *t*-BuOH and acrylonitrile at 25 °C in water-sulfuric acid mixtures [19]. About 17 % of the added *t*-BuOH was found to disappear in some uninvestigated side reaction, other than the formation of TBAA, accompanied by a significant lowering of the acidity of the reaction mixture. It now seems clear that the unidentified product was AMPS which has been lost by its simple solubilization in the aqueous solution of sulfuric acid used.

CONCLUSIONS

The data reported here confirm the ease of selective preparation of *N*-tert-butylacrylamide from the Ritter reaction between tert-butylalcohol and acrylonitrile in the presence of concentrated sulfuric acid, in excess anhydrous acetic acid or acrylonitrile, by properly adjusting the reaction conditions.

N-tert-butylacrylamide is the main reaction product up to 50 °C with 80-98 wt % sulfuric acid concentration.

The reaction follows second-order kinetics up to 50 % conversion with rates proportional to the increasing quantity of sulfuric acid added.

A significant transformation of the resulted amide to the water-soluble monomer AMPS, by sulfonation, takes place only at higher temperatures and especially with fuming sulfuric acid.

SYMBOLS AND ABBREVIATIONS

t-BuOH:	tert-Butylalcohol
ACN:	Acrylonitrile
AcOH:	Acetic acid (anhydrous)
SA:	Sulfuric acid with or without free

	SO ₃
AMPS:	2-Acrylamido-2-methylpropane-sulfonic acid
H ₂ SO ₄ (^{an}):	Unreacted sulfuric acid
H, h:	Hammett acidity function
ε:	Molar absorptivity
hr:	Hours
min:	Minutes

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