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T. Partha Sarathy[a]; K. Nageswar Rao[a]; B. Sethuram[a]; T. Navaneeth Rao[a]
[a] Department of Chemistry, Osmania University, Hyderabad, India

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NOTE

A KINETIC STUDY OF THE PHOTOPOLYMERIZATION OF *N,N* METHYLENEBISACRYLAMIDE INITIATED BY *N*-BROMOSUCCINIMIDE IN THE PRESENCE AND ABSENCE OF ISOPROPYL ALCOHOL

T. PARTHA SARATHY, K. NAGESWAR RAO,* B. SETHURAM, and
T. NAVANEETH RAO

Department of Chemistry
Osmania University
Hyderabad 500007, India

ABSTRACT

The photopolymerization of *N,N'*-methylenebisacrylamide has been studied with *N*-bromosuccinimide as photoinitiator in the presence and absence of isopropyl alcohol (ISP). The rate of polymerization in the presence of ISP was found to be very high, and this is explained on the basis of the relative reactivities of the initiating radicals. A probable mechanism consistent with the observed results is proposed and discussed.

INTRODUCTION

N-Bromosuccinimide (NBS) is a well-known two-electron oxidant under thermal conditions [1, 2]. An ionic mechanism has been suggested for the oxidation of variety of organic compounds by NBS [1]. However, under photochemical conditions, NBS undergoes homolytic fission, giving rise to bromine and succinimidyl radicals. Ghosh and Mitra [3] investigated the photopolymerization of methyl methacrylate and other vinyl monomers with NBS as photoinitiator, and reported that both bromine and succinimidyl radicals are capable of initiating the polymerization. In the present study the rate of polymerization of *N,N'*-methylenebisacrylamide (MBA) by NBS increased with the addition of isopropyl alcohol (ISP). This prompted us to investigate the role of ISP in the polymerization.

EXPERIMENTAL

All the reagents used were of AnalaR grade. MBA (Aldrich) was recrystallized from hot water. *N*-Bromosuccinimide (BDH) solutions were prepared fresh just before use. Isopropanol (BDH) was purified by the method of Wells and Davies [4]. Photolysis was carried out with a medium-pressure mercury lamp (UVS 500 Hanovia). Pyrex glass vessels were arranged so that their distance from the lamp was the same. Standard ferrioxalate actinometry was employed for measuring the light intensity. Before irradiation, the sample solution was deaerated by bubbling with oxygen-free nitrogen for 15 min. After irradiation, the reaction mixture was filtered through a G_4 sintered glass crucible, dried at 30°C for 1 day, and weighed. The reactions were carried out at 25°C in an aqueous medium.

RESULTS AND DISCUSSION

Effect of NBS Concentration on the Polymerization Rate

The rate of polymerization increased with an increase in [NBS], and the order in [NBS] was found to be 0.4 and 0.5 in the presence and absence of ISP, respectively (Figs. 1 and 2). This fractional order dependence on [NBS] indicates that the polymerization is initiated by primary radicals with termination by mutual reaction of two growing polymer radicals. Primary radical termination is eliminated since this would cause the order in [NBS] to be zero.

Effect of MBA Concentration on the Polymerization Rate

The rate of polymerization increased with the concentration of monomer. The order in [MBA] was found to be 1.2, both in the presence and the absence of ISP (Figs. 1 and 2). If the termination were affected by primary

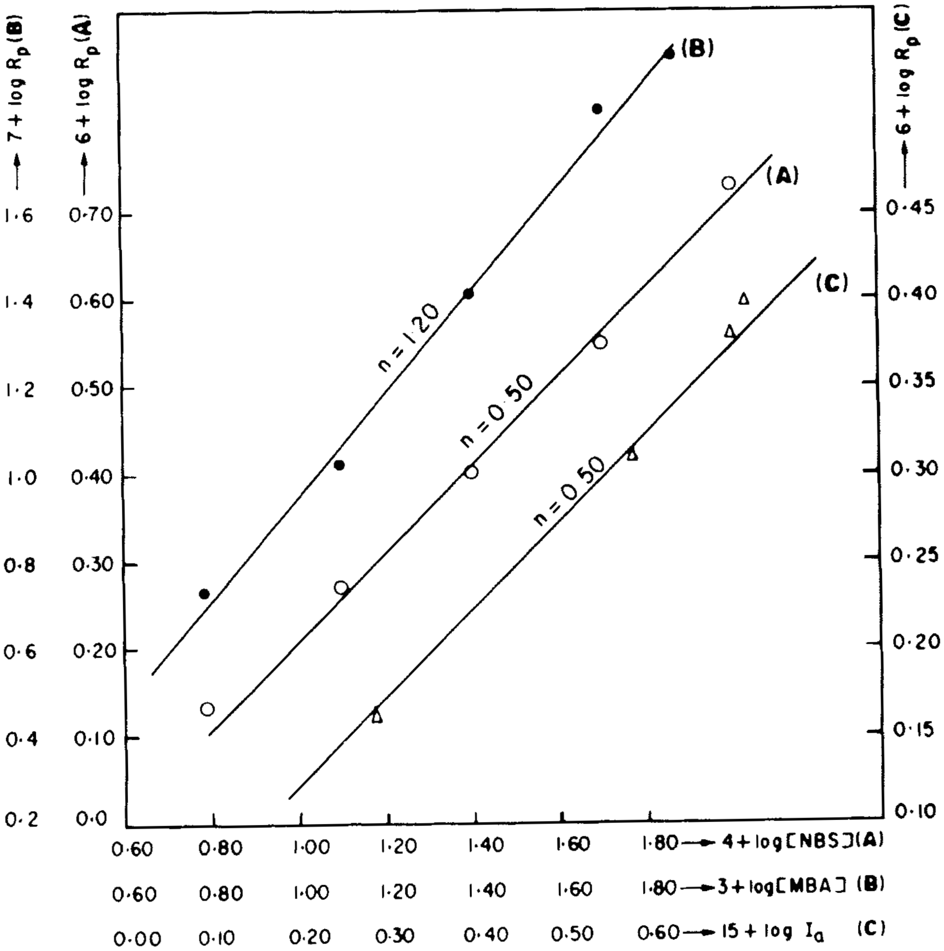


FIG. 1. Plot of (A) log [NBS], (B) log [MBA], and (C) log I_a vs log R_p. [MBA] = 25 mmol/L; [NBS] = 2.50 mmol/L; I_a = 5.40 × 10^{15} quanta/(L•s); temperature, 298 K.

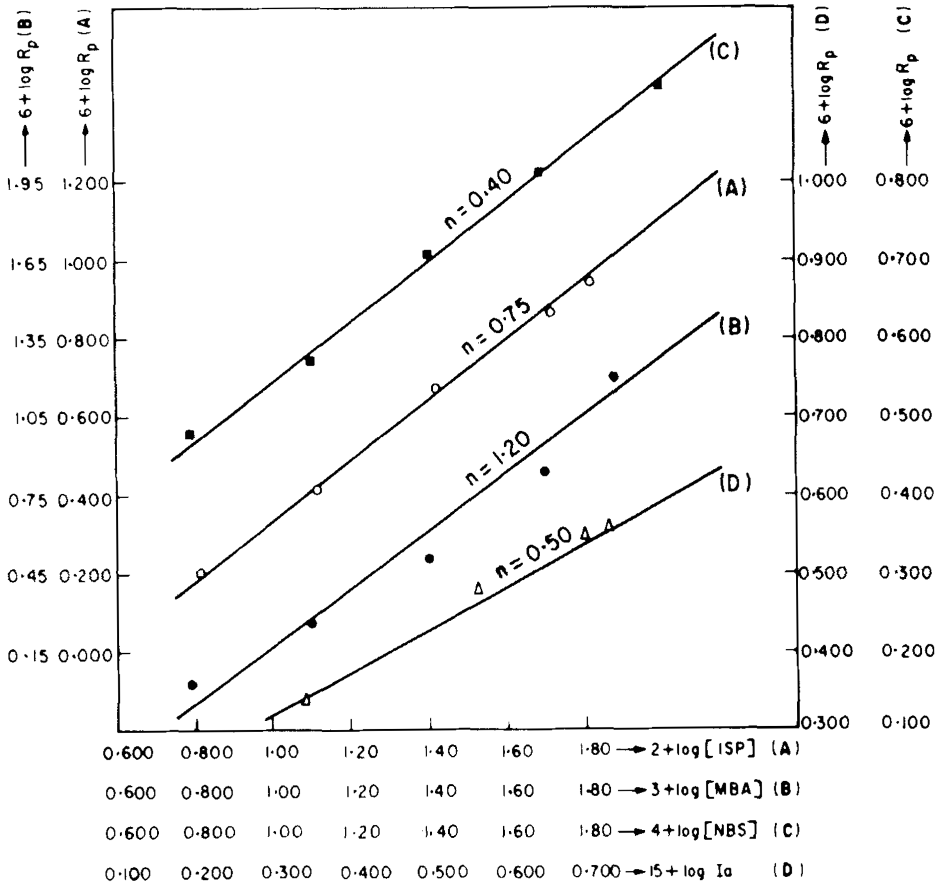


FIG. 2. Plot of (A) log [ISP], (B) log [MBA], (C) log [NBS], and (D) log I_a vs log R_p. [MBA] = 25 mmol/L; [NBS] = 2.50 mmol/L; [ISP] = 131 mmol/L; I_a = 5.40 × 10^{15} quanta/(L·s); temperature, 298 K.

radicals, the order in [MBA] should be 2.0. Since this order was not observed, mutual termination appears most probable.

In the present case the cyclopolymerization mechanism is operative since the resulting polymer was soluble in a water-pyridine mixture and the IR spectra of the polymer showed the absence of double bonds [5].

TABLE 1. Rates of Polymerization[a]

Time, min	Without ISP, $R_p \times 10^6$, mol/(L•s)	With ISP, $R_p \times 10^6$, mol/(L•s)
25	1.30	2.81
30	1.80	3.69
35	2.30	3.78
40	2.57	3.51
45	2.67	3.36
50	2.81	3.13

[a] [MBA] 25 mmol/L, [NBS] = 2.50 mmol/L, [ISP] = 131 mmol/L, I_a = 5.40 × 10^{15} quanta/(L•s), temperature 298 K.

Effect of Intensity on the Polymerization Rate

The rate of polymerization increased with the light intensity, and the order in intensity was 0.5 both in the presence and the absence of ISP (Figs. 1 and 2). This dependence also supports mutual termination.

Effect of ISP Concentration on the Polymerization Rate

The rate of polymerization increased with increasing [ISP], and the order in [ISP] was found to be 0.75 (Fig. 2). This fractional order also shows that mutual termination is operative.

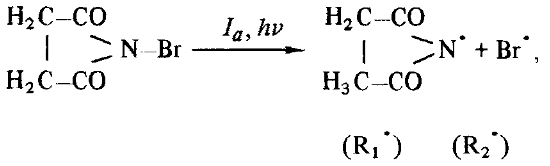
Mechanism

The rate of polymerization of the MBA-NBS system was found to increase on addition of isopropyl alcohol (Table 1). This must be due to an increase in the rate of production of initiating radicals. Photolysis of NBS in the presence of ISP probably produces ketyl radicals in addition to bromine and succinimidyl radicals. It is reported in the literature [6-8] that the succinimidyl radical is highly reactive, with selectivity similar to that of chlorine atom. It behaves as an electrophile [9] due to the presence of two electron-withdrawing acyl groups adjacent to the nitrogen. Since the chlorine atom is more reactive than the bromine atom, the succinimidyl radical is assumed to be much more reactive than bromine. This radical was also reported [9] to be more capable of attacking the double bond than the bromine atom.

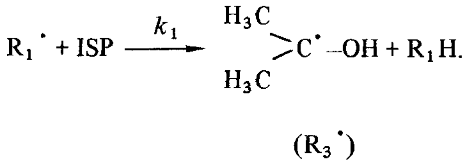
The succinimidyl radical not only attacks the double bond but is also a very good hydrogen-abstracting species [10, 11]. It is also known that these radicals undergo dimerization [12, 13]. The high rate of polymerization in the presence of ISP compared to its absence could be due to the production of ketyl radicals by the reaction of succinimidyl radicals with ISP instead of succinimidyl radicals undergoing dimerization. The UV spectra of the reaction mixture shows peaks at 213, 227 and 241 nm, which correspond to succinamide formed by abstracting hydrogen from the reducing agent, i.e., isopropanol. The absence of the peaks (222, 230, and 246 nm) corresponding to dimer in the presence of ISP and the presence of these peaks in the absence of ISP also supports this conclusion. The production of ketyl radicals was proved by the IR spectra of the resulting polymer, which showed a peak at 3600 cm^{-1} corresponding to O–H. Acetone was detected by its characteristic reaction with salicylaldehyde in a basic medium which gives a red complex that can be formed only from ketyl radicals.

On the basis of above results and discussion, the following mechanism is suggested.

Primary radical generation:



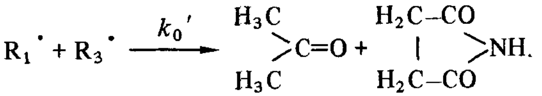
$$\begin{matrix}H_2C-CO\\ |\quad >N-Br\\ H_2C-CO\end{matrix} \xrightarrow{I_a,\,h\nu} \underset{(R_1^{\bullet})}{\begin{matrix}H_2C-CO\\ |\quad >N^{\bullet}\\ H_3C-CO\end{matrix}} + \underset{(R_2^{\bullet})}{Br^{\bullet}}, \tag{1}$$



$$R_1^{\bullet} + ISP \xrightarrow{k_1} \underset{(R_3^{\bullet})}{\begin{matrix}H_3C\\ \quad >C^{\bullet}-OH\\ H_3C\end{matrix}} + R_1H. \tag{2}$$

Radical deactivation:

$$2R_2^{\bullet} \xrightarrow{k_0} R_2-R_2, \tag{3}$$



$$R_1^{\bullet} + R_3^{\bullet} \xrightarrow{k_0'} (H_3C)_2C{=}O + \begin{array}{c} H_2C{-}CO \\ | \\ H_2C{-}CO \end{array}\!\!>\!NH. \tag{4}$$

Initiation:

$$R_1^{\bullet} + M \xrightarrow{k_i} M_1^{\bullet}, \tag{5}$$

$$R_2^{\bullet} + M \xrightarrow{k_i'} M_1^{\bullet}, \tag{6}$$

$$R_3^{\bullet} + M \xrightarrow{k_i''} M_1^{\bullet}. \tag{7}$$

Cyclization:

$$M_1^{\bullet} \xrightarrow{k_c} M_c^{\bullet}. \tag{8}$$

Propagation:

$$M_c^{\bullet} + M \xrightarrow{k_p} M_{c+1}^{\bullet}. \tag{9}$$

Termination:

$$(M_c^{\bullet})_m + (M_c^{\bullet})_m \xrightarrow{k_t} \text{polymer}. \tag{10}$$

On applying the steady-state approximation, the rate law in the absence of ISP becomes

$$R_p = k_p \left\{ \frac{I_a k_i [\text{NBS}]\,[\text{M}]}{k_t (k_i[\text{M}] + k_0)} \right\}^{1/2} [\text{M}], \tag{11}$$

and in the presence of ISP becomes

$$R_p = \frac{k_p}{k_t} \left\{ \frac{k_1 I_a [\text{NBS}]\,[\text{ISP}]}{k_1\,[\text{ISP}] + k_i[\text{M}]} + \frac{k_i'' k_1^{\,2}\,[\text{M}]\,[\text{ISP}]^2}{k_0'(k_1\,[\text{ISP}] + k_i[\text{M}])} \right\}^{1/2} [\text{M}]. \tag{12}$$

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