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RADICAL-INDUCED DECOMPOSITION OF DIMETHYL-*N*-(2-CYANO-2-PROPYL)KETENIMINE

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ABSTRACT

The decomposition of 2,2′-azobisisobutyronitrile (AIBN) and dimethyl-*N*-(2-cyano-2-propyl)ketenimine (**1**) were studied using a radical scavenger, 1,1,3,3-tetramethylisoindolin-2-yloxyl (**2**), to isolate the cage reaction. Anomalous results were obtained, and these are explained by an induced decomposition of the ketenimine (**1**) by the radical scavenger (**2**), which results in an increased rate of decomposition and a change in the ratio of combination:disproportionation products. A mechanism for the induced decomposition is proposed.

INTRODUCTION

2,2′-Azobisisobutyronitrile (AIBN) has been an initiator of choice for many studies because of its freedom from induced decomposition as is evident by the first-order decomposition observed. An additional reason to study AIBN decompositions is that the cyanoisopropyl radicals formed are a simple model for the polymerization of methacrylonitrile (MAN). Recent studies [1] from our group have shown that the termination reaction of cyanoalkyl radicals involves competition between C—C and C—N coupling, analogous to that observed in the formation of ketenimine (**1**) from AIBN. More importantly, where unsymmetrical coupling is

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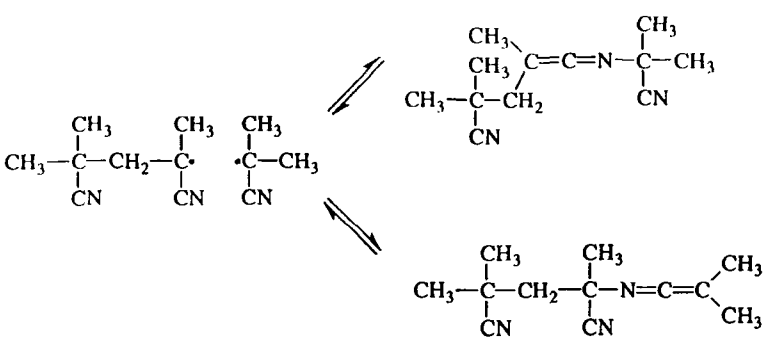
possible (Scheme 1), we observed selectivity and a dependence of this selectivity on the β-substituent. These observations prompted us to present a more detailed study of AIBN and ketenimine (1). It is well known that in the thermolysis of AIBN [2], significant C—N coupling occurs. It is also accepted [3] that ketenimine (1) is an alternate source of cyanoisopropyl radicals. It has been proposed [4] that ketenimines are way stations in many thermal and photochemical decompositions of azonitriles. Therefore, it is of some importance that a study of AIBN should involve that of ketenimine (1).

The breakdown of AIBN and ketenimine (1) involves a different cage reaction. In their respective decomposition, the transition state of AIBN involves a nitrogen molecule whereas that of ketenimine (1) does not. As a consequence, the spatial distributions of the radicals generated are different. The closer proximity of the radicals generated from ketenimine (1) makes it easier for the radicals to self-terminate by either combination or disproportionation in the solvent cage, i.e., the cage effect, than is the case for radicals from AIBN. As a result of the larger cage effect, the initiator efficiency of ketenimine (1) was generally found [3, 5] to be much lower than that for AIBN. In the case of AIBN, the distance between the radicals generated is greater, hence the radicals have a longer time and therefore an increased chance to diffuse out of the solvent cage.

Any differences observed, particularly in the combination:disproportionation (c:d) ratio between AIBN and ketenimine (1), may well be attributable to the importance of the cage effect. This is related to the ability of the radicals to escape the solvent cage, which in turn is a function of viscosity, among other things. The conversion of monomer to polymer and the accompanying increase in viscosity could also affect cage reactions. Therefore, an understanding of the cage effect may also allow for a greater understanding of polymerization reactions.

It is the aim of this present study to determine the product composition and kinetics in the decomposition of both AIBN and ketenimine (1), with special emphasis on the amount of cage reaction and the composition of the cage and encounter products. The use of a radical scavenger, 1,1,3,3-tetramethylisoindolin-2-yloxyl (2), allows the cage reaction to be studied in isolation by trapping any radicals that had escaped the solvent cage, i.e., the encounter radicals, as nitroxide adducts. The decomposition of AIBN will be undertaken by both thermolysis and photolysis



SCHEME 1.

whereas that of the ketenimine (1) can only be carried out by thermolysis because it is stable under the photolytic conditions used.

EXPERIMENTAL

Materials

Commercially available AIBN (Schering Industrial Chemicals, UK) was purified by recrystallization from ethanol. The ketenimine (1) was obtained by photolysis of AIBN according to the method of Smith et al. [7]. 1,1,3,3-Tetramethylisoindolin-2-yloxyl (2) was prepared from *N*-benzylphthalimide by reaction with methylmagnesium iodide in toluene, followed by hydrogenolysis and oxidation, according to the method of Griffiths et al. [8]. Benzene was dried over sodium and purified by distillation. Isobutyronitrile (IBN) and MAN (Aldrich) were purified by standard procedures [9]. Tetramethylsuccinonitrile (TMSN) was obtained by the method of Smith et al. [10].

Kinetic Measurements

The determination of the rate of decomposition was undertaken by nuclear magnetic resonance (NMR) spectrometry in the absence of the radical scavenger. However, this method is inappropriate when used with the radical scavenger because of interference in the NMR signals by the paramagnetic nature of the radical scavenger. High performance liquid chromatography (HPLC) was used as an alternative method. A 10% solution of AIBN or ketenimine (1) in benzene-d_6 (0.5 mL) was introduced into a NMR tube, degassed by three freeze–evacuate–thaw cycles, and sealed under a vacuum of 10^{-3} mmHg. An initial NMR spectrum was recorded on a Jeol FX-90Q or GX-400 spectrometer. The solution was either photolyzed by a 450W Oriel Xenon arc lamp or thermolyzed by immersion in a Haake F3 constant temperature bath.

Several NMR spectra were recorded over the period of the reaction by quenching the reaction at predetermined intervals. The rate constant for the decomposition was calculated by linear regression analysis of ln [*A*] vs time, where *A* is the integral of the peak corresponding to AIBN or the ketenimine (1).

In the presence of a radical scavenger (2), the kinetic measurement was carried out with HPLC by measuring the area under the AIBN peak for a number of identical reaction mixtures, quenched at different time intervals. HPLC was undertaken on a Waters model 510 system equipped with a Phenomenex C_{18} reverse phase column and two detectors, an Isco V^4 UV-Vis detector and a Waters model 410 Refractive Index detector, connected in series. A typical run involved a 10% sample in methanol (10–80 μL) eluted at 2 mL/min with either methanol or 85% methanol in water. The products were compared to known concentrations of authentic samples.

Product Determination

A solution of AIBN or ketenimine (1) (50 mg) and the radical scavenger (2) (100 mg) in benzene (0.5 mL) was introduced into a flask fitted with an Embell vacuum tap. The solution was degassed by three freeze–evacuate–thaw cycles, sealed

under vacuum, and the flask immersed in the constant temperature bath at 80°C for at least 10 half-lives of the reaction.

The products were analyzed by reverse-phase HPLC after removal of benzene in vacuo, and the residue was taken up in methanol. The products were separately analyzed by capillary GC using a Hewlett-Packard 5890A gas chromatograph equipped with an ultra-high crosslinked methyl silicone gum stationary phase and attached to a HP3396A integrator. GC analyses were performed by the use of a temperature program of 25°C (10 minutes), ramp rate at 5°C/min, to 200°C (10 minutes). Each reaction was performed in duplicate, and the c:d ratio of the products, TMSN and IBN, was the average of at least three GC determinations. Detector response factors were determined from known concentrations of authentic samples.

RESULTS AND DISCUSSION

Kinetics

The first-order rate constants for the decomposition of AIBN and the ketenimine (**1**) in benzene at 80°C were found by NMR study to be 1.57×10^{-4} and 1.60×10^{-4} s^{-1}, respectively. These values for the rate constants are consistent with those obtained from previous studies [2, 11].

In the presence of a radical scavenger, the decomposition of AIBN was found to still exhibit first-order kinetics, with a typical value for the rate constant of 1.49×10^{-4} s^{-1} from HPLC determination being comparable to that found in the absence of the radical scavenger. On the other hand, the decomposition of the ketenimine (**1**) showed a greatly increased rate and does not appear to exhibit *n*-order kinetics. This would imply a mechanism with a competing reaction in operation during the course of the decomposition. Attempts are currently being made to elucidate this mechanism.

We propose that the acceleration in the decomposition of the ketenimine (**1**) is attributed to radical-induced decomposition by the radical scavenger. Support for this observation is obtained with the results from the product determination to be discussed later.

Product Determination

The Cage Effect

The products from the decomposition of AIBN or the ketenimine (**1**) in the presence of the radical scavenger (**2**) were analyzed by HPLC. The radical scavenger (**2**) (t_r = 6.37 minutes) and the nitroxide adduct (t_r = 7.01 minutes) have distinct retention times. At a wavelength of 270 nm, the radical scavenger and the nitroxide adduct have very similar molar absorptivities [12], and as such the relative amount of each can be determined from the integral of their respective peaks in the HPLC chromatograms. Furthermore, excellent correlations were obtained between the results from this method and that from isolation of the products by column chromatography. The relative percentage of cage and encounter reactions are shown in Table 1.

TABLE 1. Percent Cage and Percent Encounter Reactions in the Thermolysis of AIBN and the Ketenimine (1) in the Presence of the Radical Scavenger (2)

Reactants	Cage	Encounter
AIBN	42	58
(1)	60	40

The data in Table 1 show that the efficiency of free-radical production from ketenimine (1) is significantly lower than from AIBN. This had been previously reported [3, 5] to be due to the different spatial distributions of the radicals in the solvent cage for AIBN and ketenimine (1).

Combination:Disproportionation Ratios

The relative amounts of TMSN and IBN in each reaction mixture were determined by capillary GC. As with previous work [13], MAN was not analyzed as such but the amount of (IBN and MAN) is taken to be 2 × IBN. The results are summarized in Table 2. In the absence of the radical scavenger (2), the total reaction, which is taken to be the sum of the cage and encounter reactions (Eq. 1), is measured.

$$\text{(total reaction)} = \text{(cage reaction)} + \text{(encounter reaction)} \quad (1)$$

The thermal decompositions of AIBN and of the ketenimine (1) without the radical scavenger (2) show very similar c:d ratios, with combination being the predominant mechanism for termination. With an uncertainty of around ±5% in measurements, any difference between the results for AIBN and the ketenimine (1) in the absence of (2) must be seen to be within the bounds of experimental errors.

TABLE 2. Percent c:d Ratios from the Complete Decomposition of AIBN and the Ketenimine (1)

Reactants	Method of decomposition	(1)[a]	TMSN	IBN and MAN[d]
AIBN	$h\nu$[b]	50.6	47	2.4
AIBN	Δ[c]	–	90	10
(1)	Δ[c]	–	94	6
AIBN and (2)	Δ[c]	–	68	32
(1) and (2)	Δ[c]	–	39	61

[a]Determined by ^{1}H NMR.
[b]Photolysis with a xenon arc lamp at a distance of 15 cm.
[c]Thermolysis by immersion in a constant temperature bath at 80°C.
[d]Disproportionation products (IBN and MAN) are taken to be 2 × IBN.

In light of the large cage effect observed for the ketenimine (1) in Table 1 and the assertion by Minato et al. [6] that a pair of unsymmetrical radicals would tend to favor disproportionation, this result is somewhat surprising. It was expected that the ketenimine (1) would give a larger amount of disproportionation products, and hence a lower c:d ratio, than is actually obtained.

In the photolysis of AIBN, the amount of the ketenimine (1) obtained is consistent with earlier studies in other solvents [3, 5]. Discounting the high proportion of the ketenimine (1) obtained, the c:d ratio is found to be similar to that for the thermolysis of AIBN. Since the photolysis was carried out at room temperature (~22°C), there appears to be no significant thermal dependence (in the 22–80°C range) of the c:d ratio.

Previous studies [3, 5, 14, 15] have primarily concentrated on the cage effect as a function of the total reaction rather than the c:d ratio in the cage reaction itself. This is a point of vital concern in polymerization of species where there is a transient termination step, as is the case of the ketenimine (1) in the decomposition of AIBN.

The results in Table 2 show that disproportionation is favored over combination in the cage reaction from the decomposition of the ketenimine (1) whereas the converse is true for AIBN. Although this observation is consistent with results previously reported [3, 5], the c:d ratios appear to be substantially lower than expected, considering first the high c:d ratio for the total reaction seen in Table 2 for both AIBN (90:10) and the ketenimine (1) (94:6), and second the previously reported results of the c:d ratio of the cage reaction being similar to that of the encounter reaction (16, 18].

The initial assumption in the present study was that the radical scavenger (2) does not play a direct part in the decomposition reactions, and that its only role is to trap any radicals that have escaped the solvent cage, i.e., the encounter radicals. In other words, the basis for studying the products of the cage reaction is Eq. (1), and it must hold to give meaningful results. The results from Tables 1 and 2 are combined, according to Eq. (1), to give Table 3.

It is immediately obvious from Table 3 that the large "negative" value for disproportionation in the encounter reaction of the ketenimine (1) means that Eq. (1) does not hold in this case. Hence, the large negative value in the c:d ratio of Eq. (1) must be attributed to a much larger amount of disproportionation products obtained from the cage reaction by this method than is possible by the normal

TABLE 3. Uncorrected Results for the Absolute c:d Ratios of the Cage and Encounter Reactions

Reactants	Total	Cage[a]	Encounter[b]
AIBN	90:10	29:13	61:−3
(1)	94:6	23:37	71:−31

[a]Calculated from the percentage of the cage effect (Table 1) and the percent c:d ratio for the cage reaction (Table 2).

[b]Encounter = total − cage.

termination mechanism alone. This suggest that an additional mechanism is operating in the trapping of the encounter radicals.

The failure in this method can either stem from the measurement of the cage effect or the determination of the c:d ratios. As the percent cage reaction measured both by the amount of the nitroxide adduct obtained and the radical scavenger recovered gave similar results, it is inconceivable that both results were subjected to the same degree of error. As such, it is more probable that a lower than expected c:d ratio from what was thought to be the cage reaction alone resulted in the negative value. It follows then that this mechanism must be favorable toward the formation of disproportionation products. It also follows that since the radical scavenger is the only variable from the total reaction, the assumption that radical scavenger (2) plays no direct part in the decomposition also does not hold. It is proposed that the mechanism involves a radical-induced decomposition of the ketenimine (1) by the radical scavenger (2).

In the case of AIBN, the results obtained are within reasonable experimental errors when the encounter reaction is assumed to be comprised predominantly or totally of combination, which is probable, given that cyanoisopropyl radicals tend to favor combination in a random termination.

Radical-Induced Decomposition

One of the reasons for preferring the use of AIBN over benzoyl peroxide is that the latter is subjected to secondary dissociation and induced decomposition, among other reactions, that complicate vinyl polymerization [19, 20]. The mechanism of radical-induced decomposition of benzoyl peroxide (R—R) by a propagating radical (P.) can best be summed up by

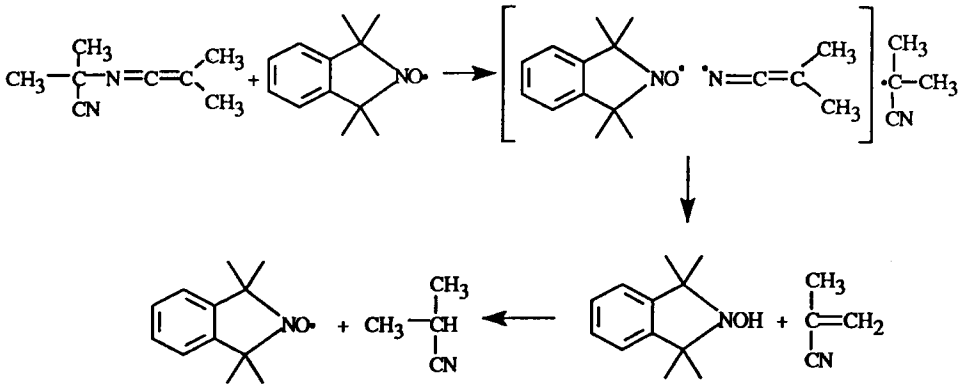
$$R—R + P. \rightarrow R. + R—P \qquad (2)$$

No induced decomposition of AIBN or the ketenimine (1) by the cyanoisopropyl or the keteniminyl radicals was detected in this study nor was it previously reported. However, an induced decomposition could conceivably occur without being detected because the products generated are the same as the reactants.

It has been shown [16] for dimethylazobisisobutyrate that the nitroxide adduct may thermally decompose in situ to form a molecule of hydroxylamine and one of methyl methacrylate. Furthermore, this hydroxylamine in turn can donate its hydrogen atom to a 1-methoxycarbonyl-1-methylethyl radical to reform the radical scavenger as well as produce a molecule of methyl isobutyrate.

We propose a similar mechanism for the ketenimine (1), but at an accelerated rate, to account for the increase in disproportionation products (Scheme 2). This increased rate may be due to an induced decomposition of the ketenimine (1) by the radical scavenger.

In a related example, C.-H. S. Wu et al. [14] found that the rate of decomposition of *N*-(1-cyanocyclohexyl)pentamethyleneketenimine is significantly accelerated in the presence of scavengers. The mechanism we propose involves a ketenimine-radical scavenger complex, followed by formation of a molecule of hydroxylamine and one of MAN, and finally regeneration of the radical scavenger and formation of a molecule of IBN.



SCHEME 2.

CONCLUSIONS

The decomposition of AIBN and the ketenimine (1) were found to self-terminate predominantly by combination. Simple first-order kinetics were followed for both AIBN ($k = 1.57 \times 10^{-4}$ s^{-1}) and the ketenimine (1) ($k = 1.60 \times 10^{-4}$ s^{-1}). In the absence of a radical scavenger, this is a measurement of the total reaction, which is the sum of the cage and encounter reactions.

The use of the radical scavenger serves to isolate the cage reaction by scavenging any encounter radicals that had escaped the solvent cage. This cage reaction was found to comprise 42 and 60% of the total reaction for AIBN and the ketenimine (1), respectively. Furthermore, it was found that the c:d ratio in the cage reaction for AIBN, and particularly for the ketenimine (1), is significantly lower than that for their corresponding total reactions.

Whereas the results for AIBN may be rationalized, those for the ketenimine cannot be explained by the normal reaction mechanism alone. Hence, it was proposed that the higher percent disproportionation may be due to a radical-induced decomposition of the ketenimine (1) by the radical scavenger (2), which would lead to formation of more IBN and MAN. This additional mechanism is supported by the accelerated rate of disappearance of the ketenimine (1) in the presence of (2).

Further studies are underway to elucidate the details of the radical-induced decomposition of ketenimine. In this connection, ^{13}C-labeled ketenimine is being studied.

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