Oxidation of Diphenylmethanol by Bromamine T. A Kinetic and Mechanistic Study †

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Bromamine T (BAT) oxidises diphenylmethanol and substituted diphenylmethanols smoothly and quantitatively to the respective benzophenones in aqueous acetic acid. Mineral acids catalyse the reaction and the rate law is found to be $-d[BAT]/dt = k[BAT][Alcohol][H^+]$. The reaction is characterised by the absence of any kinetic isotope effect and a break in the Hammett plot with ρ values of -4.2 and -0.4 for the two limbs. Three alternative mechanistic pathways have been proposed involving (i) diphenylmethyl cation, (ii) a 'phenonium ion' type intermediate from the decomposition of the alkyl hypobromite ester, or (iii) *ipso* substitution at the benzene ring followed by dehydrobromination and aromatization.

Considerable attention has been focused on the chemistry of halogens and related *N*-halogeno-*N*-metallo-reagents,[1-5] but little work is on record on the use and reactions of bromamine T (BAT) as an oxidant, although the reactions of its chlorine analogue, chloramine T (CAT), have been extensively studied.[6] To rectify this situation, the kinetics of oxidation of diphenylmethanol and its substituted derivatives have been studied in aqueous acetic acid media in order to elucidate the nature of the oxidising species and mechanism.

Results

The oxidation of diphenylmethanol by BAT proceeds smoothly and the reaction is found to be clearly of first order both with respect to time (as evidenced by good fits of log [BAT] *versus* time plots) and concentration as shown by the time order rate coefficient being independent of initial concentration of BAT (Table 1). The effect of variation of initial concentration of diphenylmethanol (Table 1) and hydrogen ion (Table 2) shows first-order dependence on the concentration of both alcohol and acid. The rate law under these conditions is (1).

$$-d[BAT]/dt = k[BAT][Alcohol][H^+] \qquad (1)$$

Effect of Added $NaClO_4$ *and Toluene*-p-*sulphonamide*.—Addition of neutral salts such as perchlorate enhances the rate but slightly and initially added toluene-*p*-sulphonamide (TSA) retards the rate of the reaction (Table 3).

Effect of Solvent Polarity.—The reaction is retarded by increasing the volume percentage of acetic acid in $HOAc-H_2O$ mixtures (Table 4).

Kinetic Isotope Effect.—The degree of carbon–hydrogen bond rupture in the rate-determining step can be determined by measuring the primary hydrogen–deuterium isotope effect. It is observed that both [α-^{2}H]diphenylmethanol and 2,2′-dimethyl[α-^{2}H]diphenylmethanol are oxidised at the same rates as their corresponding protio-compounds (Table 5) in contrast to the oxidation of alcohols by molecular halogen[7,8] and *N*-halogeno-compounds[9,10] under similar conditions.

Table 1. Effect of concentration of reactants at 50 °C

$10^2[Ph_2CHOH]$/M	10^3[BAT]/M	10^4k_{obs} [a]/s^{-1}
1.0	1.0	1.78
1.5	1.0	2.67
2.0	1.0	3.56
2.5	1.0	4.46
3.0	1.0	5.28
4.0	1.0	7.00
2.5	2.0	4.43
2.5	2.5	4.47
2.5	3.1	4.45

Solvent 70% HOAc (v/v), [$HClO_4$] 1.0 × 10^{-2}M

[a] Rate constants are accurate to ±3%.

Table 2. Effect of hydrogen ion concentration at 30 °C

	10^4k_{obs}/s^{-1} for catalysis by	
$10[H^+]$/M	H_2SO_4	$HClO_4$
1.5	3.93	9.02
2.5	6.57	15.1
3.0	7.85	18.0
5.0	13.2	30.1
6.0	15.8	36.0
7.5	19.7	45.2

[Ph_2CHOH] 1.0 × 10^{-2}M, [BAT] 1.0 × 10^{-3}M, solvent 70% HOAc (v/v)

Table 3. Effect of added $NaClO_4$ and TSA at 50 °C

[$NaClO_4$]/M	10^3[TSA]/M	10^4k_{obs}/s^{-1}
0.1		3.62
0.2		3.81
0.3		3.90
0.4		4.03
	0.50	3.12
	0.75	3.01
	1.00	2.85
	1.50	2.62
	2.50	1.95

[Ph_2CHOH] 2.0 × 10^{-2}M, [BAT] 1.0 × 10^{-3}M, solvent 70% HOAc (v/v), [$HClO_4$] 1.0 × 10^{-2}M

Structural Effects.—Structural modifications in the phenyl moiety result in varied reactivity; while electron-releasing substituents accelerate the rate of oxidation to a very large extent, the rate retardation by electron-withdrawing groups though perceptible is not very high. A Hammett analysis of the substituent effects made in the Figure brings out the important difference of this oxidation reaction when compared

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Table 4. Effect of solvent polarity at 50 °C

% HOAc (v/v)	$10^5k_{obs}/s^{-1}$
30	54.6
40	34.4
50	29.8
60	22.6
70	17.8
80	14.8
90	9.92

[Ph_2CHOH] 1.0 × 10^{-2}M, [BAT] 1.0 × 10^{-3}M, [$HClO_4$] 1.0 × 10^{-2}M

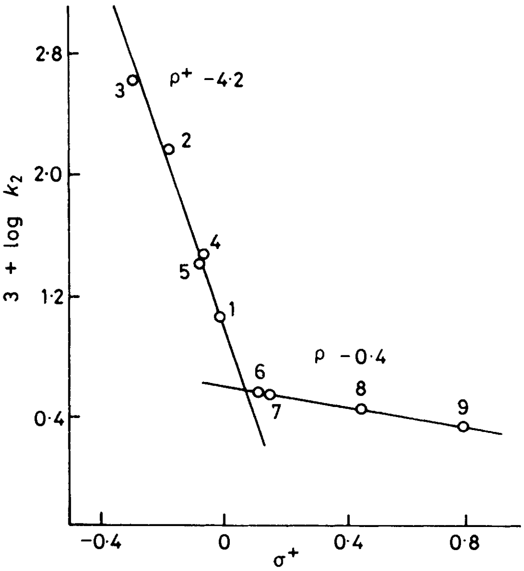
Table 5. Kinetic isotope effect at 50 °C

Substrate	10^2k_2/l mol^{-1} s^{-1}	k_H/k_D
Diphenylmethanol	1.78	
[α-^{2}H]Diphenylmethanol	1.69	1.05
2,2′-Dimethyldiphenylmethanol	13.2	
2,2′-Dimethyl[α-^{2}H]diphenylmethanol	13.2	1.02

[BAT] 1.0 × 10^{-3}M, solvent 70% HOAc (v/v), [$HClO_4$] 1.0 × 10^{-2}M

with the similar systems studied earlier. The oxidation of alcohols by *N*-bromosuccinimide has ρ −2.4 and the oxidation of fluoren-9-ols by BAT also has a similar ρ value.[11-13] On the other hand the Hammett plot shows two distinct lines, for each of which there is a good correlation between the substituent constants and the logarithm of the rate constants particularly when σ$^+$, the Okamoto–Brown constant,[12] is used for the electron-releasing substituents. Of these one has a much larger ρ of −4.2 and the other a relatively low ρ of −0.4 at 40 °C (Figure).

Effect of Temperature.—The rate data on temperature effects in aqueous acetic acid media have been studied in the range 313—333 K and the activation parameters calculated from the least-square slopes of log k_2 *versus* $1/T$ are presented in Table 6.



Hammett plot for the reaction of diphenylmethanol and X-substituted diphenylmethanol *versus* bromamine T at 40 °C. Solvent 70% HOAc (v/v), [BAT] 1.0 × 10^{-3}, [$HClO_4$] 1.0 × 10^{-2}M; 1, X = H; 2, X = 4-Ph; 3, X = 4-Me; 4, X = 3-Me; 5, X = 4-F; 6, X = 4-Cl; 7, X = 4-Br; 8, X = 3-Br; 9, X = 4-NO_2

Table 6. Activation parameters

Diphenylmethanol substituent	$\Delta H^{\ddagger\,a}$/kcal mol^{-1}	$-\Delta S^{\ddagger\,b}$/cal mol^{-1} K^{-1}
H	10.5	34.3
4-Ph	5.6	44.6
4-Me	4.4	46.5
3-Me	13.4	23.0
4-F	6.3	46.3
4-Cl	14.6	23.2
4-Br	15.4	20.6
3-Br	17.7	13.9
4-NO_2	20.4	5.8

[a] At 40 °C; the maximum error is 0.5 kcal mol^{-1}. [b] At 40 °C.

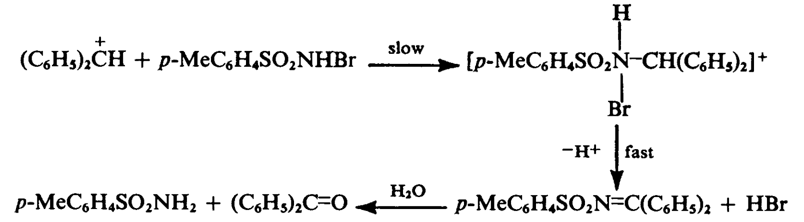
Discussion

Nature of the Oxidising Species.—In a solution of bromamine T in aqueous acetic acid the reactive species are likely to be BAT, $BATH^+$, Br_2, HOBr, Br^+, H_2O^+Br, CH_3COOBr, and $CH_3CO\overset{+}{O}(H)Br$; hence the oxidation in this case may be a reaction between an alcohol molecule and one of the above species. (i) The rate-retardation on the initial addition of TSA indicates the reactive species is formed along with TSA from BAT in a fast equilibrium step prior to the rate-determining step. (ii) In the case of *N*-bromo-compounds such as *N*-bromosuccinimide (NBS), Br^+ is proposed as an effective oxidant.[13] The thermodynamic calculations by Bell and Gelles,[14] however, have shown that a stripped halogen cannot exist in appreciable concentration in aqueous solution. (iii) Langbein and Steinert [15] proposed molecular bromine (formed in an autocatalytic reaction) as the oxidising species in the NBS oxidation of propan-2-ol. The rate of the reaction with propan-2-ol was found to be independent of NBS concentration but first order with respect to initially added Br_2 concentration. But, in the present study, the reaction rate has a clean first-order dependence on [BAT] at all conditions for over 75% of the reaction. Further, the reaction is not complicated by the accumulating Br^- ions. Thus, BAT does not undergo any autocatalytic reaction to yield Br_2. However, in the presence of a large quantity of initially added bromide ions, Br_2 is likely to be the reactant. (iv) *N*-Bromo-compounds are known to be excellent sources of hypobromous acid,[16] and this can be formed by the nucleophilic attack of water. Under acidic conditions, the formation of hypobromous acidium ion is further facilitated. (v) The possibility of the formation of an acyl hypobromite in acetic acid solutions has been documented.[17] A nucleophilic attack of HOAc on BAT may lead to the generation of BrOAc. Thus of the several alternatives the most likely oxidants in the solvent system employed are the unprotonated species, *viz*., HOBr and CH_3COOBr as shown by the dependence of the reaction rate on acidity and on TSA. The equilibria (2) and (3) preceding the slow step would account for the observed rate retardation when TSA is added to the system.

$$C_7H_7SO_2\bar{N}Br + H_3O^+ \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} C_7H_7SO_2NHBr + H_2O \quad (2)$$

$$C_7H_7SO_2NHBr + H{-}X \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} TSA + X{-}Br \quad (3)$$

$$X = OH \text{ or } CH_3COO$$



$$(C_6H_5)_2\overset{+}{C}H + p\text{-}MeC_6H_4SO_2NHBr \xrightarrow{\text{slow}} [p\text{-}MeC_6H_4SO_2\overset{H}{\underset{Br}{N}}\text{-}CH(C_6H_5)_2]^+ \quad (6)$$

$$\downarrow \text{fast}, -H^+$$

$$p\text{-}MeC_6H_4SO_2NH_2 + (C_6H_5)_2C{=}O \xleftarrow{H_2O} p\text{-}MeC_6H_4SO_2N{=}C(C_6H_5)_2 + HBr \quad (7)$$

Scheme 1.

Mechanism of Oxidation.—The experimentally observed rate law requires the involvement of one molecule of the alcohol and the X-Br molecule and yet the reaction should not involve the cleavage of the α-C-H bond; also it should be susceptible to polar effects and should account for the Hammett plot which is biphasic.

A priori, diphenylmethanol could react in a different way from the related alcohols benzyl alcohol, phenylmethylcarbinols, and fluoren-9-ols because of the established fact that diphenylmethanol and diphenylmethyl derivatives are capable of dissociating into the diphenylmethyl cation and the counter-ion. Burton and Cheesman[18] while studying the action of mineral acids such as HCl or $HClO_4$ on the dismutation of diphenylmethanol established reactions (4) and (5) in this system. Therefore, one should take into account the

$$(C_6H_5)_2CHOH + H^+ \rightleftharpoons (C_6H_5)_2CH\overset{+}{O}H_2 \rightleftharpoons (C_6H_5)_2\overset{+}{C}H + H_2O \quad (4)$$

$$(C_6H_5)_2\overset{+}{C}H + (C_6H_5)_2CHOH \rightleftharpoons (C_6H_5)_2CH\text{-}O\text{-}CH(C_6H_5)_2 + H_2O \quad (5)$$

formation of the diphenylmethyl cation as well as the bisdiphenylmethyl ether as intermediates. However, the formation of the latter has necessarily to be a side reaction and bisdiphenylmethyl ether is not likely to be involved in the oxidation reaction proper, for in this case one would have observed a second-order dependence on the concentration of alcohol. The diphenylmethyl cation formed might, however, interact with the BAT molecule according to Scheme 1.

Scheme 1 envisages a slow interaction between the diphenylmethyl cation and the oxidant itself (instead of the X-Br) and has an analogy in the proposal of Ruff *et al.* on the Mann–Pope reaction (the oxidation of dialkyl sulphides to dialkyl sulphoxides by CAT).[19,20] The foregoing proposal would accommodate the experimental observations if one assumes that the interaction between the diphenylmethyl cation and the oxidant is the slow step and the subsequent break-up of the intermediate is a fast one. For, the formation of diphenylmethyl cation in the prior step would be governed by the presence or absence of electron-releasing substituents (leading to a large negative ρ) and the concentration of the cation will be related directly to the nature of such a substituent. Whereas electron-withdrawing substituent in the *meta*- or *para*-positions would not facilitate the formation of the cation and would lead to a rate almost equivalent to that of the present compound (with a consequent break in the Hammett plot). Since the subsequent dehydrobromination takes place in a fast step and does not involve the cleavage of the α-C-H bond, the reaction would not exhibit any isotope effect.

$$C_7H_7SO_2NHBr + H\text{-}X \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} TSA + X\text{-}Br \quad (3)$$

$$Ph_2CHOH + X\text{-}Br \underset{k'_{-2}}{\overset{k'_2}{\rightleftharpoons}} Ph_2CHOBr + HX \quad (8)$$

$$Ph_2CHOBr \xrightarrow[k_3]{\text{slow}} Ph_2C{=}O + HBr \quad (9)$$

Scheme 2.

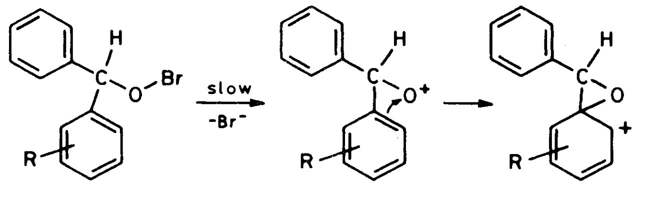
An alternative proposal (Scheme 2) involves the slow decomposition of hypobromite ester intermediate in the rate-determining step, leading to a rate law (10). Although this mechanism resembles that of Deno and Potter[21] for the Br_2 oxidation of propan-2-ol, there must be considerable differences in the bond-breaking processes in order to account for

$$\text{rate} = k_3K_2K_2'[Ph_2CHOH][BAT][H^+] \quad (10)$$

the lack of kinetic isotope effect and the differential Hammett plot. The decomposition of the hypobromite ester can have any of the following characteristics depending upon the nature of the alcohol moiety: (i) considerable E_1 character, (ii) considerable E_2 character, and (iii) borderline of E_1 and E_2 character. According to Deno and Potter, the driving force for the decomposition of such an ester is the effective removal of the α-hydrogen atom as a proton by the solvent water, functioning as a base. Since the bromide ion is a better leaving group, the driving force in the present case may be considered as cleavage of the O-Br bond with the liberation of Br^- leaving behind a residual positive charge on the oxygen atom. The creation of such a positive charge on the oxygen atom which is highly electronegative is in turn relayed to the α-carbon atom or has to be quenched by the assistance offered by a neighbouring group. The former situation would lead to the cleavage of the α-C-H bond in the slow step which will not be in agreement with the lack of any isotope effect in the reaction. An alternative proposition, by analogy with the substitution reactions of β-phenylethyl derivatives, is participation by the neighbouring phenyl group. Thus, the decomposition of hypobromite ester intermediate may be accelerated by anchimeric assistance by a phenyl group to an electron-deficient oxygen atom in the rate-determining step as in Scheme 3.

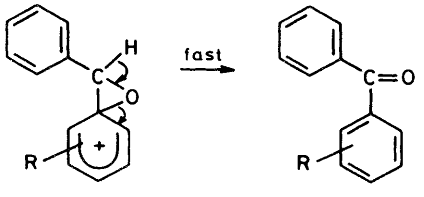
The ‘ phenonium ion ’ (I) could be resonance stabilized and may decompose in a fast step as in Scheme 4. The intermediate (I) postulated in this mechanism is the oxygen analogue of the ‘ phenonium ion ’ proposed by Cram in the solvolysis of β-arylalkyl tosylates.[22]

The negative reaction constant indicates a considerable magnitude of carbonium ion character in the transition state. The generation of a carbonium ion is possible either by electrophilic attack on the α-carbon of the substrate or by the removal of α-hydrogen as a hydride ion. The former possibility can be ruled out since such an attack on a saturated carbon is highly unlikely. The latter option should also be untenable in this instance since the reaction exhibits negligible



(I)

Scheme 3.



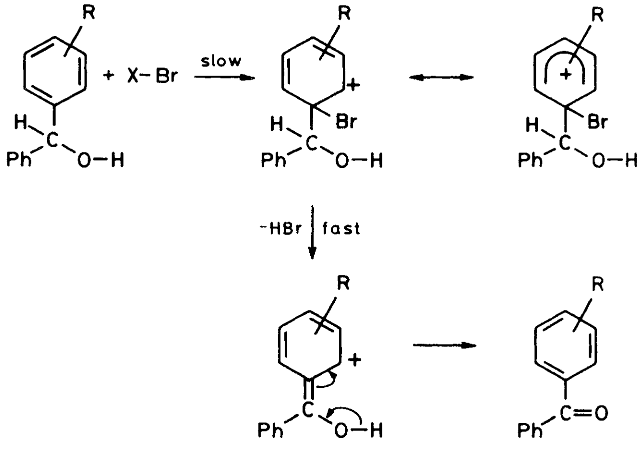
(I)

Scheme 4.

primary kinetic isotope effects. The above proposal, however, locates the positive charge first at one of the phenyl rings and then at the α-carbon atom. The positive charge associated with the mesomeric ion (I) will be stabilized by electron-releasing groups in the phenyl ring as long as there is such a substituent in the system. Thus, of the two phenyl groups in the diphenylmethanol molecule, it is the one with electron-releasing substituents that readily provides the anchimeric assistance for the formation of the ' phenonium ion ' intermediate. But when electron-withdrawing substituents are present it is the unsubstituted phenyl ring which involves itself in neighbouring group participation. As a result, in the latter case, the rate of oxidation changes but slightly (ρ −0.4 at 40 °C) with the change in the substituents. There is yet another mechanism (Scheme 5) that seems to satisfy the experimental observations in the present investigation. The oxidant, *viz.*, X–Br, is also an effective electrophilic reagent. The oxidation of an aromatic system such as diphenylmethanol can be regarded as proceeding *via* an initial *ipso*-substitution by the electrophilic reagent at the phenyl carbon atom adjacent to the α-carbon atom followed by a rapid dehydrobromination and aromatization (Scheme 5).

The correlation of the experimentally determined rate constants with the Okamoto–Brown constants indicates considerable charge development in the phenyl rings and would thus be in accord with Scheme 5. The three proposals are in agreement with the lack of any isotope effect both in the case of diphenylmethanol and also in the more hindered alcohol 2,2′-dimethyldiphenylmethanol. That the latter compound reacts faster than the unsubstituted compound by about eight times can only be explained if one assumes relief of steric strain on going to the product 2,2′-dimethylbenzophenone. And yet such relief does not involve the α-C–H bond in the slow step. As this molecule can still form a ' phenonium ion like ' intermediate in view of the 6 and 6′-positions being free, the reaction could still proceed while not involving the α-C–H bond, resulting in the absence of a kinetic isotope effect. The rate enhancement with increasing polarity of the solvent medium could be explained on the basis of the more polar nature of the transition state envisaged in the mechanisms. Nevertheless, it must be admitted that, at the moment, it is difficult to choose among the above three proposals.

It is interesting to note that similar results have been obtained earlier in the NBS oxidation of diphenylmethanol [23]



Scheme 5.

(ρ −2.79 for electron-releasing substituents and −0.45 for electron-withdrawing substituents; k_H/k_D 1.1 at 40 °C). A plot of log k_2 (NBS) *versus* log k_2 (BAT) is linear, underscoring the fact that both the oxidations follow a similar mechanistic pathway.

Experimental

Bromamine T was prepared from dibromamine T (DBT) which in turn was prepared by the bromination of chloramine T.[24–26]

(i) Chloramine T (10 g) (Société des usines chimiques Rhône) of extra pure quality was dissolved in water (200 ml) in a two-necked flask (250 ml) fitted with a funnel. Liquid bromine (AnalaR) (2 ml) was added dropwise while the contents of the flask were stirred using a magnetic stirrer for 1 h. The golden yellow precipitate of DBT was then removed, washed thoroughly with water, filtered under suction, and dried in a vacuum desiccator for 24 h. The dry sample was found to melt at 92—93 °C with decomposition.

(ii) DBT (8 g) was then dissolved in small lots at a time and with stirring in an alkaline solution (2 g of sodium hydroxide in 15 ml of water). The contents were cooled in ice when pale yellow crystals of BAT separated out. They were filtered off under suction, washed quickly with a minimum quantity of water, and dried (P_2O_5) (yield 7 g).

(iii) T.l.c. (Acme grade silica gel, 0.5 mm; 1 : 1 EtOAc–hexane) analysis yielded a single spot confirming the formation of a single product. The purity of the compound was estimated to be 99% by iodometric procedures [27] and other spectral data.

The substituted diphenylmethanols were prepared by the reduction of the corresponding benzophenones [28] using sodium borohydride (B.D.H.). Substituted benzophenones were prepared by Friedel–Crafts reaction of suitably substituted benzoyl chlorides with benzene. Reduction of 4-nitrobenzophenone with $NaBH_4$, however, did not give the desired product. Therefore, the reduction of the ketone has been carried out using a fresh solution of aluminium isopropoxide which was prepared as cited.[29] [α-^{2}H]Diphenylmethanol was prepared by refluxing dry sodium methoxide, zinc dust (AnalaR) and benzophenone in D_2O (Bhabha Atomic Research Centre). The purity of the compounds was checked by n.m.r., i.r., and mass spectra. AnalaR grade acetic acid was used after purifying by the usual procedure.[30] All the inorganic chemicals used were of AnalaR grade. Solutions of diphenylmethanol and BAT were prepared in HOAc–H_2O mixtures and were thermostatted for 2 h before each run and

50 ml of each solution were mixed. Portions (5 ml) of the reaction mixture were pipetted out at regular intervals and quenched in 5% KI solution (5 ml). 2N-H_2SO_4 (10 ml) was added and the liberated iodine was titrated against standard thiosulphate to a starch end-point. The reactions were carried out under pseudo-first-order conditions. The first-order rate coefficients were evaluated using the integrated rate expression. In the evaluation of rate coefficients the kinetics were followed to nearly 75% reaction. The stoicheiometry (11) of the reaction was obtained by taking a known excess of BAT over alcohol at 40 °C in 0.5M-H_2SO_4. Benzophenone was estimated as its 2,4-dinitrophenylhydrazone derivative. The reaction

$$Ph_2CHOH + C_7H_7SO_2\bar{N}Br \longrightarrow C_7H_7SO_2NH_2 + Br^- + Ph_2CO \quad (11)$$

mixtures failed to induce polymerisation of acrylonitrile and the effect of nitrogen on the reaction was also negligible.

Acknowledgements

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