Gamma Radiation Induced Formation of Iodine Monochloride in Iodine in Some Aromatic Chlorinated Solvents

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Abstract: Gamma radiation induced formation of ICl in aerated and deaerated solutions of iodine in some aromatic chlorinated solvents has been studied for different concentrations and γ dosages. G values for formation of ICl and decomposition of I_2 were determined in gamma radiolysis of aerated and deaerated solutions of I_2 in 1,2-dichlorobenzene(1,2-DCB), 1,3-dichlorobenzene(1,3-DCB), 2-chlorotoluene, 3-chlorotoluene and benzotrichloride. G(ICl) values have been found to decrease in the following order 2-chlorotoluene < 3-chlorotoluene < 1,2-DCB < 1,3-DCB < benzotrichloride. G(ICl) is slightly higher in aerated solutions than in deaerated solutions and is found to be dependent on the structure of the parent organic molecule.

Keywords: Aromatic chlorinated solvents, Iodine monochloride, *G*-value

Introduction

In recent years, the addition of reactive solutes to liquids being irradiated has been extensively applied as a technique for scavenging free radicals intermediates. The radical scavenging using I_2 in various chlorinated organic solvents has been a subject of detailed investigations[1-5] in the past. However, no detailed study has been studied in aromatic chlorinated solvents.

In the present work, we have investigated gamma radiation induced formation of ICl in 1,2-DCB, 1,3-DCB, 2-chlorotoluene, 3-chlorotoluene and benzotrichloride at different concentrations of I_2 in presence and absence of oxygen.

Experimental

All the chemicals used were of AR grade. Freshly prepared solutions of I_2 of 0.4 mM, 0.8 mM and 1.2 mM in aromatic chlorinated solvents as mentioned above were air saturated for 15 min prior to irradiation.

The steady-state irradiations were carried out with Cobalt-60 Gamma Chamber - 900 housed in Nuclear Chemistry laboratory, Department of Chemistry, Rashtrasant Tukadoji

Maharaj Nagpur University, Nagpur. The dose rate of the Co-60 source during the course of work was ~ 0.5kGy/h. The dose rate was measured using Fricke dosimetry with G (Fe^{3+}) = 15.6. Dose correction for aromatic chlorinated solvents was applied using expression:

$$D_M = D_D \frac{(Z/A)_M}{(Z/A)_D} \tag{1}$$

Where Z/A is the mean ratio of sum of atomic numbers and molecular weight of the medium and the dosimeter solution respectively. An aliquot of each solution was exposed to successively increasing dosages depending on the appearance of ICl. Stoppered irradiation cells made of corning glass and standard B-19 joints were used to minimize solvent evaporation. Post irradiation absorbance spectra were recorded on Elico SL 210 Double beam UV-Visible spectrophotometer. The spectra of unirradiated sample solutions were recorded simultaneously. The same method was carried out for solutions of I_2 (0.8mM) through which N_2 was passed for 15 minutes prior to irradiation.

Results and Discussion

The visible spectra of non-irradiated solutions of I_2 in aromatic chlorinated solvents mentioned above exhibit characteristic maxima at ~515 nm showing presence of I_2. However, after irradiation, I_2 starts disappearing with subsequent appearance of new characteristic maxima indicating the formation of ICl. These spectra cross with each other at the isobestic point indicating the presence of two species I_2 and ICl simultaneously. Typical absorption spectra for different concentrations of I_2 at various dosages are shown in Figure 1.
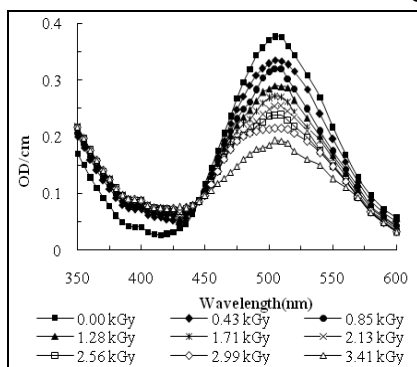
Figure 1. Absorption spectra of I_2 solution in 2-chlorotoluene at different dosages for 0.4 mM initial I_2 concentration

Spectral characteristic of solutions of I_2 in chlorinated solvents are given in Table 1.

Table 1. Spectral characteristic of I_2 solutions in various aromatic chlorinated solvents

| Solvents	Absorption maxima of I_2 λ_{max} nm	Absorption maxima of ICl λ_{max} nm	Isobestic point of I_2 and ICl nm
1,2-DCB	510	425	450
1,3- DCB	510	420	440
2-Chlorotoluene	505	400	445
3-Chlorotoluene	505	395	440
Benzotrichloride	510	440	450

The formation of ICl and disappearance of I_2 at increasing dosages were calculated from two simultaneous equations[5,6].

$$[Abs]_{430} = 40.6\ [I_2] + 128\ [ICl] \tag{2}$$

$$[Abs]_{515} = 918\ [I_2]\ + 59.8\ [ICl] \tag{3}$$

Where, absorbance values were directly obtained from spectra. The amount of ICl formed and I_2 decomposed at different irradiation dosages were calculated using equations (2) and (3) and plotted to give yield dose curves. It was observed that as the concentration of I_2 in chlorinated solvents increases, the dose required to convert iodine into ICl also increases. Figure 2 shows a plot of absorbed dose required for formation of ICl from I_2 in 1,2-DCB, 1,3-DCB, 2-chlorotoluene, 3-chlorotoluene and benzotrichloride.
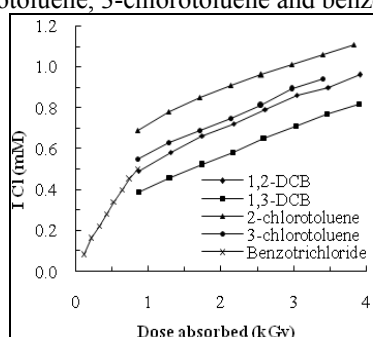
Figure 2. Correlation of dose absorbed and ICl formed from I_2 in 1,2-DCB, 1, 3-DCB, 2-chlorotoluene, 3-chlorotoluene and benzotrichloride

A linear relationship with good coefficient of correlation (R=0.991, 0.998, 0.988, 0.997 and 0.996 for 1,2-DCB, 1,3-DCB, 2-chlorotoluene, 3-chlorotoluene and benzotrichloride respectively) was observed. Thus, it is inferred that ICl formation from I_2 in aromatic chlorinated solvents varies directly as the function of absorbed dose.

Variation of G(–I_2) and G(ICl) with dose absorbed

A summary of variation of G(-I_2) and G(ICl) for different concentrations of I_2 in aromatic chlorinated solvents is given in Table 2.

Table 2. Variation of G(-I_2) and G(ICl) values at various I_2 concentrations in different aromatic chlorinated solvents

Solvent	Initial Conc. of I_2 mM	Absorbed dose (kGy)	G(-I_2)	G(ICl)	Δ ICl/Δ I_2
		Aerated			
1,2-DCB	0.4	0.49	3.65	18.58	
		0.98	2.42	9.29	
		1.47	0.94	6.91	1.66
		1.95	0.82	6.07	
	0.8	0.87	3.57	16.10	
		1.31	0.90	14.92	
		2.18	0.15	10.97	1.83
		3.48	0.22	8.58	

		0.87	3.37	15.38	
	1.2	2.18	0.90	11.73	1.91
		3.05	0.32	10.42	
		3.92	0.20	8.98	
		0.43	4.53	18.73	
	0.4	0.86	1.81	11.16	1.92
		1.30	0.45	8.16	
		1.73	0.11	6.30	
		0.87	4.07	16.17	
1,3-DCB	0.8	1.30	1.05	13.42	1.83
		2.17	0.63	10.49	
		2.60	0.30	9.46	
		0.87	4.29	15.41	
	1.2	1.73	1.02	13.30	1.61
		2.60	1.43	11.26	
		3.90	0.25	8.07	
		0.43	2.29	21.16	
	0.4	0.85	1.38	14.23	2.00
		1.28	0.31	10.46	
		1.71	0.24	8.57	
		0.85	2.53	20.47	
2-Chlorotoluene	0.8	1.28	1.53	18.52	2.00
		1.70	1.15	16.64	
		2.98	0.13	11.60	
		0.85	2.30	18.66	
	1.2	2.98	0.46	10.87	1.86
		3.40	0.23	10.15	
		3.83	0.10	9.27	
		0.85	2.07	21.22	
	0.4	1.28	0.61	14.88	
		1.70	0.46	12.07	
3-Chlorotoluene		2.13	0.18	10.24	2.00
		0.85	3.45	20.11	
	0.8	1.28	1.23	16.33	
		2.55	0.46	10.60	
		2.98	0.20	9.72	1.86
		0.85	3.68	18.29	
	1.2	1.28	2.30	17.56	
		2.55	0.77	13.17	
		3.40	0.23	10.70	1.76
		0.07	5.40	24.49	
	0.4	0.14	2.78	24.35	
		0.21	2.75	23.37	
Benzotrichloride		0.43	1.11	22.28	1.76
		0.11	6.41	23.95	
	0.8	0.21	5.61	23.45	1.85
		0.74	1.19	21.64	
		0.85	1.01	20.00	

Contd...

	1.2	0.14	6.97	23.89	1.82
		0.28	6.86	22.97	
		1.13	1.38	19.76	
		1.27	0.92	19.30	
	Deaerated				
1,2-DCB	0.8	0.85	1.84	13.90	1.57
		1.28	1.38	12.68	
		1.70	0.92	12.25	
		2.13	0.46	11.85	
1,3-DCB	0.8	0.84	2.33	14.43	1.50
		1.26	1.86	11.59	
		2.10	0.37	8.29	
		2.94	0.20	6.56	
2-Chlorotoluene	0.8	0.85	3.93	15.47	1.91
		2.11	0.74	10.31	
		2.54	0.39	9.21	
		3.38	0.12	7.27	
Benzotrichloride	0.8	0.21	9.23	16.16	1.63
		0.42	6.00	15.42	
		0.85	0.69	14.69	
		0.90	0.62	13.71	

The plots of radiation chemical yield (*G*-values) and dose absorbed in various aromatic chlorinated solvents has been compared as shown in Figure 3.
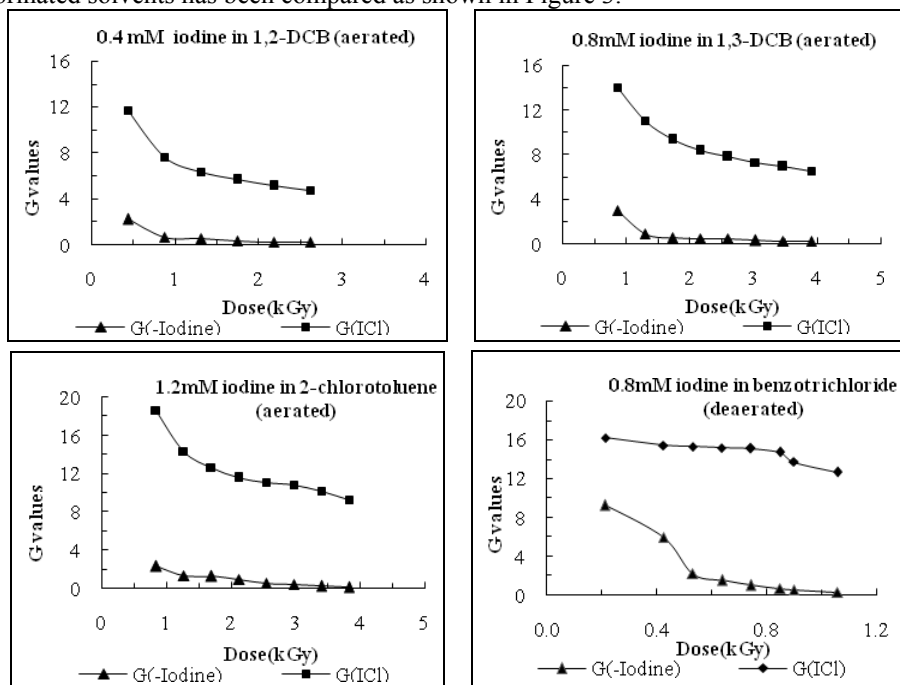
Figure 3. Variation of $G(-I_2)$ and $G(ICl)$ with dose absorbed in aerated 1,2-DCB, 1,3-DCB, 2-chlorotoluene and deaerated benzotrichloride

From Figure 3, it is observed that $G(-I_2)$ and $G(ICl)$ values decrease with increase in concentration due to decrease in number of ICl molecules formed with increasing concentration of I_2. As the number of Cl atoms available for formation of ICl at higher concentration of I_2 becomes less, it is quite likely that less number of ICl molecules are formed at higher I_2 concentrations. It is noticed that G values suddenly drop at higher dosages. Presumably, at higher dosages, a part of ICl is getting decomposed and it reaches to saturation value.

The formation of ICl and $^\bullet$Cl as one of the products was observed by Bibler[8,9] in radiolysis of air-saturated solution of I_2 in CCl_4. In the present work, radiolysis of I_2 solutions in aromatic chlorinated solvents also results in ICl as the major product due to radical reaction.

In aromatic chlorinated solvents, very high dose is required to effect a colour change and for formation of ICl, a part of energy gets deposited on benzene ring which is resonance stabilized and hence, Ar-Cl bond is not broken easily. The dose required to effect colour change and for formation of ICl in $C_6H_5CCl_3$ is less as compared to $C_6H_4Cl_2$ and Cl $C_6H_4CH_3$ as Cl in $C_6H_5CCl_3$ is not directly attached to benzene ring.

In case of I_2 in chlorobenzenes, ICl is the main product containing iodine although very small amounts of C_6H_6, $C_6H_5C_6H_5$, $C_6H_5C_6H_5Cl$, C_6H_4ICl and C_6H_5I ($G < 0.5$) have also been detected[10,11]. The primary dissociation reaction may take place directly through dissociation of excited molecules or indirectly through ionic intermediates[12]. Radiolysis of chlorotoluenes possibly lead to ionization, excitation and electrons react by dissociative electron attachment[13].

There may be formation of several other products like HCl, higher chlorohydrocarbons or oxides of chlorine but these were not identified. The possibility of chain reaction mechanism cannot be ruled out due to high $G(ICl)$ values. Due to certain constraints of the experimental set up in our laboratory, the formation of other products could not be identified.

Thus, it is observed that in radiolysis of aromatic chlorinated compounds at one stage or the other, $^\bullet$Cl is one of the products formed as a result of carbon-halogen and carbon-hydrogen bond rupture[14]. It seems that presence of aromatic ring does not stabilize the aromatic chlorinated compounds towards radiolysis.

Radiolysis of I_2 in 1,2-DCB, 1,3-DCB, 2-chlorotoluene, 3-chlorotoluene and benzotrichloride solutions under aerated conditions gives significantly higher $G(ICl)$ than in absence of oxygen. This additional yield possibly derives due to the addition of molecular oxygen to the radicals generated by the reactions of the primary radiation-induced radicals, e^- with the respective aromatic chlorinated solvents[15,16].

Conclusion

The concentration of ICl varies linearly with the dose absorbed at lower dosages with good coefficient of correlation. After a certain dose, a deviation in $G(-I_2)$ and $G(ICl)$ values are observed for every solvent and each concentration. This could be due to C-Cl bond dissociation energy.

The observed values of $G(ICl)$ in presence of oxygen were found to be slightly higher than those in absence of oxygen due to the addition of molecular oxygen to the radicals generated by the reactions of the primary radiation-induced radicals, e^-, with the respective aromatic chlorinated solvents.

G(-I₂) and G(ICl) are found to be almost constant for every solvent and each iodine concentration. Radiolytic decomposition of I_2 in aromatic chlorinated solvents and formation of ICl is observed to be dependent on the structure of the parent organic molecule.

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