

**Kinetics & Mechanism of Halogenative
Oligomerization of Mesityl Oxide by
Chloramine-T: Evidence for a Novel Pathway
in Aqueous Sulphuric Acid***

S. VIVEKANANDAN, K. VENKATARAO & M. SANTAPPA
Department of Physical Chemistry, University of Madras
Guindy Campus, Madras 600025

and

Sr. SUBRAMOGANATHAN
Department of Chemistry, Pachaiyappa's College
Madras 600030

Received 26 April 1978; accepted 23 May 1978

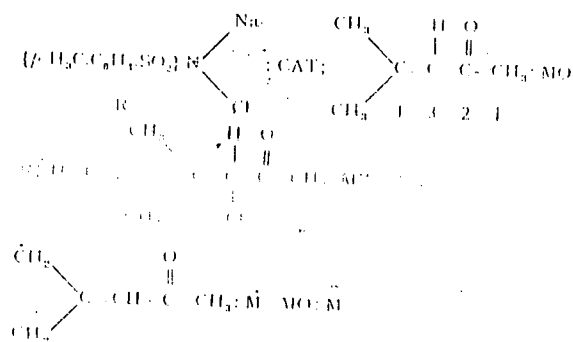
The kinetics of the reaction between mesityl oxide and chloramine-T (CAT) in aqueous sulphuric acid in the presence of KHSO_4 has been studied. The results indicate a radical chain mechanism to be operative which is quite novel in CAT kinetics.

CHLORAMINET (CAT) has established itself as an efficient and dependable oxidant and a versatile chlorinating agent in chemical analysis^{1,2} and in reaction kinetics^{3,4}. Only simple products have been noticed so far in its reaction with

*Presented as a preliminary report at the All India seminar on *Oxidation-reduction reactions* held at the University of Madras, January 1978 and with further results presented as a paper at the *Chemistry symposium* held at the IIT, Madras, March 1978.

substrates^{3,4}. We report in this communication our kinetic evidence for a novel halogenative oligomerization of mesityl oxide (MO) by chloramine-T in aqueous (0.375M) sulphuric acid.

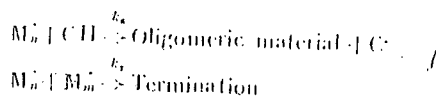
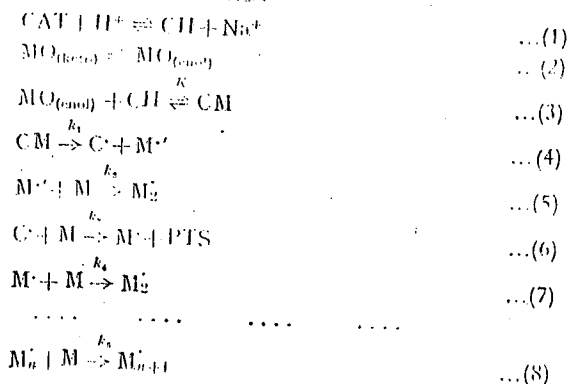
In the presence of KHSO_4 , the reaction manifests a typical fractional order behaviour, i.e. a clean 1.5 order in [CAT] and a 0.5 order at low [MO] ($<0.015M$) which changes to zero order under pseudo conditions (1:15). This is quite familiar in free radical polymerization kinetics. Besides this Michaelis-Menten type of behaviour, the reaction is associated with very fast equilibria during the initial stages. This kinetic evidence for complex formation is supported by the large shifts in the λ_{max} values for the reaction mixture when compared to those of the reactants. A negligible salt effect (μ : 0.477M to 0.777M; k at 40°: 0.219 to 0.267M^{-0.6} sec⁻¹) and a marginal increase in rate with increasing $[\text{H}_3\text{O}^+]$ (0.113M to 0.375M; k at 40°: 0.244 to 0.320M^{-0.6} sec⁻¹) have been noticed. This behaviour indicates that the ionic mechanism postulated in reactions involving CAT^o may not be operative under our kinetic conditions. The reaction is considerably faster in the absence of added mineral acids suggesting an altogether different mechanism. Initially added Cl₂ has a marked influence on the rate which could be explained by its oxidation to Cl⁻ that helps faster propagation of the chains. The overall activation energy is 64.7 kJ mol⁻¹ (35-50°; k : 0.254 to 0.958M^{-0.6} sec⁻¹). Mass law effect is not observed. Instead, the rate increases slightly with increasing initially added *p*-toluenesulphonamide (PTS) which is one of the



Scheme 1

reaction product (2.5) $10^{-4}M$ to $1 \times 10^{-3}M$, k at 40° 0.267 to $0.309M^{0.5} \text{ sec}^{-1}$. This again is in contrast to the rate suppression encountered in reactions wherein ionic mechanism is operative⁶.

Chlorinated oligomeric material were found to be the other reaction product. Further, the reaction shows variable stoichiometry clearly indicating that the nature of the reaction products markedly depends on reactant concentrations, kinetic conditions and reaction time⁷. Separate kinetic studies using dichloramine-T rule out its involvement in the kinetic scheme under our experimental conditions. Further, induced polymerization of acrylonitrile shows the involvement of free radicals in the system. All these experimental facts lead us to a radical chain mechanism (Scheme 1) which is quite novel in CAT kinetics.



The complex may be formed by the coordi-
ation of the lone pair of electrons on nitrogen
of $\text{RNH}(\text{CH}_2)$ to the C4 of MO in its enolic form.
The dissociation in M^\bullet and M_n^\bullet could be any other
other than that indicated. Statistical effect has been
taken into consideration in the hydrogen abstraction
in step (6). Assuming steady state conditions, an
expression of the type (11) could be obtained.

$$\frac{d[\text{CAT}]}{dt} = \frac{k_1 K [\text{CAT}] [\text{M}]_t}{1 + K [\text{M}]_t} - k_6 [\text{CAT}] \left\{ \frac{2k_1 K [\text{CAT}] [\text{M}]_t}{k_7 (1 + K [\text{M}]_t)} \right\}^{1/2} \dots(11)$$

where

$$K = \frac{[\text{CM}]}{[\text{CAT}]_t [\text{M}]_t} \dots(12)$$

$[\text{M}]_t \approx [\text{M}]_f$ ($l = \text{total}; f = \text{free}$)

Since the major CAT consuming step is only (9),
the first term on the right hand side of (11) will
not be significant which is in agreement with the
observed order for the reaction.

The present work indicates for the first time
the potentiality of CAT as an initiator in free
radical polymerization. Further investigations (i) on
such polymerizations, (ii) with other $\alpha\beta$ -unsaturated
systems, and (iii) in different solvent environments
are in progress.

One of the authors (S.V.) is grateful to the UGC,
New Delhi for a teacher research fellowship.

References

1. JENSEN, V. J., *CRC Crit. Rev. Anal. Chem.*, **3** (1974), 407.
2. SHANNUGANATHAN, SP. & VIVARANANDAN, S., *Indian J. Chem.*, **15A** (1977), 428.
3. MAHADEVAPPA, D. S. & NAIDU, H. M. K., *Indian J. Chem.*, **14A** (1976), 808.
4. RADHAKRISHNAMURTHI, P. S. & SAHAI, R., *Indian J. Chem.*, **15A** (1977), 700.
5. MURTHY, S. P., SANEHI, R. & AGRAWAL, M. C., *Z. Naturforsch.*, **27B** (1972), 1161.
6. KATARAJAN, M. M. & TRIAGARAJAN, V., *J. chem. Soc. Perkin II*, (1975), 1590.
7. A complete and detailed discussion of the product analysis and identification under our kinetic and other different conditions by TLC, GLC and elemental analysis and UV, IR, NMR and mass spectral studies appears elsewhere.