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Oxidation of *p*-Toluic Acid Hydrazide by Thallium(III) in Acidic Medium: A Kinetic and Mechanistic Study

AMIT VARALE and NANDINI HILAGE*
Department of Chemistry, Shivaji University, Kolhapur-416 004, India
E-mail: amitvarale@gmail.com

The kinetics of oxidation of *p*-toluic acid hydrazide by thallium(III) in a mixture of perchloric acid and hydrochloric acid medium at a constant ionic strength is carried out iodometrically. The reaction proceeds through formation of complex with reactant, which decomposes in subsequent steps to give products. The increase in [H^+] and [Cl^-] decreases the rate of the reaction. Effect of acrylonitrile shows that there is no formation of free radicals. The effect of temperature was studied at four different temperatures ranging from 15 to 30 ºC. The thermodynamic parameters were also determined and a mechanism is predicted.

Key Words: *p*-Toluic acid hydrazide, Kinetics, Thallium(III), Oxidation.

INTRODUCTION

Thallium is one of the rare elements which are widely distributed in nature. It is associated with Cu, Zn and Fe in blends and pyrites. Thallium is a soft white metal and marks paper like lead. There has been much activity in recent years concerning thallium(III) oxidations[1].

The potentialities of this oxidant are being realized more and more especially as regards the oxidation of organic compounds[2]. Hydrazides are derivatives of carboxylic acids which are easily obtained by various methods[3].

The redox potential of Tl(III)/Tl(I) couple is sensitive to the anion present in the solution. In perchloric and sulphuric acid media[4] it has the highest value of 1.23 V with either free Tl^{3+}, $TlOH^{2+}$ or thallium(III) sulphate complexes as active species, respectively. Additon of small amount of halide ions to the thallium(III) containing solution results in catalysis[5], but at higher concentrations of halide ion the rate of oxidation decreases considerably. The reason for the rate retardation is due to the decrease[6] in the redox potential (0.68 in 5 mol dm^{-3} HCl) as a result of formation of strong thallium(III) halide complexes. Therefore, thallium(III) can be utilized both as a strong(in perchloric and sulphuric media) and as a mild oxidant (in HCl medium) by changing the reactive species. Although thallium(III) has been utilized for splitting of carbon-nitrogen bonds[7], but no mechanistic investigation has been carried out. The present study deals with the kinetics and mechanism of oxidation of *p*-toluic acid hydrazide in a mixture of perchloric acid and hydrochloric acid medium.

EXPERIMENTAL

Thallium(III) solution was prepared by dissolving Tl_2O_3 (ACROS) in 1.0 mol dm^{-3} HCl and the concentration was ascertained by iodometric titration. The *p*-toluic acid hydrazide was prepared from reported procedure[8] and characterized by determining its melting point. Stock solution of *p*-toluic acid hydrazide was prepared in 50 % v/v, 1,4-dioxane. Ionic strength was kept constant.

The reactions were carried out in 50 % v/v 1-4 dioxane (SD Fine Chem.) under pseudo first order conditions keeping concentration of hydrazide in large excess over that of the oxidant. The solutions containing the reactants and all other constituents were thermally equilibrated separately, mixed and the reaction mixture was analyzed for unreacted thallium(III) iodometrically by titrating against standard thiosulphate. The pseudo-first order rate constants were determined from the slopes of linear log [Tl(III)] *vs.* time plots. The results were reproducible up to ± 5 %. Kinetic runs were followed to about three half-lives of the reactions. Under the experimental condition oxidation of 1,4-dioxane did not occur.

The stoichiometry of the reaction was determined using a known excess of thallium(III) over hydrazide and determining remaining oxidant iodometrically after 24 h. The results consistent with eqn. 1 were obtained. The corresponding carboxylic acid was characterized by determining it's m.p. (182 ºC for *p*-toluic acid)

$$\mathrm{RCONHNH_2 + 2\,Tl\,(III) + H_2O \rightarrow R\text{-}COOH + N_2 + 4H^+ + 2\,Tl\,(I)} \qquad (1)$$

RESULTS AND DISCUSSION

The reaction was carried out in a mixture of both hydrochloric acid and perchloric acid because, the reaction occurs rapidly in perchloric acid medium but in the presence of hydrochloric acid the rate is measurable. The effect of reactants on the reaction was studied at constant [HCl] and [$HClO_4$] of 0.1 mol dm^{-3} each and ionic strength of 0.3 mol dm^{-3}.

Effect of hydrazide concentration: The effect of [hydrazide] was studied between 1×10^{-2} to 1×10^{-1} mol dm^{-3}, keeping the [oxidant] constant at 3.0×10^{-3} mol dm^{-3}. It is observed that the pseudo-first order rate constant increases, with increase in [hydrazide]. The results of these runs are recorded in Table-1.

An examination of above result indicates that, the value of rate constant k depends on initial concentration of hydrazide and it increases with increase in hydrazide concentration.

Effect of thallium(III) concentration: To study the effect of thallium(III) concentration on reaction rate, concentration of oxidant was varied from 6.5×10^{-4} to 6.5×10^{-3} mol dm^{-3} keeping the [hydrazide] constant at 1×10^{-1} mol dm^{-3}. The results of these runs are recorded in Table-2.

A persual of data shows that the rate of oxidation of *p*-toluic acid hydrazide remains practically constant at five different concentrations of thallium(III). Hence, the order with respect to [oxidant] is unity.

TABLE-1
EFFECT OF HYDRAZIDE CONCENTRATION

[p-t H] M × 10^{-2}	k × 10^{-4} s^{-1}
1.0	0.90
3.0	2.10
5.0	2.91
6.4	3.27
1× 10^{-1}	4.00

TABLE-2
EFFECT OF THALLIUM(III) CONCENTRATION

T1(III) (M)	k × 10^{-4} s^{-1}
6.5 × 10^{-4}	6.51
2.0 × 10^{-3}	6.49
3.0 × 10^{-3}	6.48
5.0 × 10^{-3}	6.51
6.5 × 10^{-3}	6.50

Effect of H^+ ion concentration: To study the effect of H^+ ion concentration on the rate of oxidation of *p*-toluic acid hydrazide, the concentration of HCl was varied and also different concentrations of NaCl were added in order to keep ionic strength constant. The results of these runs are recorded in Table-3.

A persual of the above data shows that the rate of oxidation of *p*-toluic acid hydrazide decreases as the concentration of H^+ ion increases.

Effect of $Cl^–$ ion concentration: To study the effect of $Cl^–$ ion concentration on the rate of oxidation of *p*-toluic acid hydrazide by thallium(III), the concentration of HCl and $HClO_4$ were varied keeping the concentration of other reactant constant. The results of these runs are recorded in Table-4. From the above data, it shows that the rate of oxidation of *p*-toluic acid hydrazide decreases as $Cl^–$ ion concentration increases.

TABLE-3
EFFECT OF H^+ ION CONCENTRATION

$[H^+]$ (M)	k × 10^{-4} s^{-1}
7.0 × 10^{-2}	37.53
1.4 × 10^{-1}	13.05
2.8 × 10^{-1}	1.90
4.0 × 10^{-1}	0.76
5.4 × 10^{-1}	0.51

TABLE-4
EFFECT OF $Cl^–$ ION CONCENTRATION

$[Cl^–]$ (M)	k × 10^{-4} s^{-1}
7.0 × 10^{-2}	3.87
1.4 × 10^{-1}	1.38
2.8 × 10^{-1}	0.90
4.0 × 10^{-1}	0.83
5.4 × 10^{-1}	0.46

Effect of temperature: In order to determine the temperature coefficient and thermodynamic parameters, the reaction was studied at four different temperatures ranging from 15 to 30 ºC and at five different initial concentrations of hydrazide. The results of these runs are recorded in Table-5. A persual of the data clearly shows that the rates of oxidation of *p*-toluic acid hydrazide are approximately doubled for 10 ºC rise in temperature.

Effect of $NaClO_4$ concentration: In order to study the effect of $NaClO_4$ on the oxidation of *p*-toluic acid hydrazide, the concentration of $NaClO_4$ solution was varied keeping the other reactants constant. The results of these runs are tabulated in Table-6. A persual of the data from table shows that the oxidation of *p*-toluic acid hydrazide remains practically constant at five different concentrations of sodium perchlorate.

TABLE-5
EFFECT OF TEMPERATURE
[p-t H] = 3 × 10^{-2} M

Temperature (ºC)	k × 10^{-4} s^{-1}
15	1.07
20	1.50
25	2.10
30	3.10
–	–

TABLE-6
EFFECT OF $NaClO_4$
CONCENTRATION

[$NaClO_4$] M × 10^{-1}	k × 10^{-4} s^{-1}
4.4	1.53
3.6	1.50
2.8	1.52
2.0	1.48
1.2	1.53

Effect of dielectric constant: The effect of dielectric constant (D) of the medium on the rate of oxidation of *p*-toluic acid hydrazide was studied by the addition of different volumes of 1,4-dioxane (5 to 40 %) to the reaction mixture, keeping the concentration of other reactants constant. The results of these runs are recorded in Table-7. A persual of the data shows that as dielectric constant of the reaction mixture decreases rate of oxidation of *p*-toluic acid hydrazide also decreases.

Effect of acrylonitrile: In order to determine whether free radical formation takes place during the course of oxidation it was necessary to determine the effect of acrylonitrile concentration on the rate of oxidation. The reaction was carried out at five different initial concentrations of acrylonitrile. The results of these runs are recorded in Table-8. A persual of the data from table shows that the rate of oxidation of *p*-toluic acid hydrazide remains practically constant at five different concentrations of acrylonitrile. This shows that there is no formation of free radicals in the reaction.

TABLE-7
EFFECT OF DIELECTRIC CONSTANT

1,4-Dioxane	k × 10^{-4} s^{-1}
05	2.30
10	1.50
20	0.92
30	0.70
40	0.50

TABLE-8
EFFECT OF ACRYLONITRILE

Acrylonitrile (mL)	k × 10^{-4} s^{-1}
1	3.24
2	3.20
3	3.33
4	3.20
5	3.26

Since there is no formation of free radicals in the reaction, the reaction proceeds with two-electron transfer step. The order in thallium(III) was found to be unity and the order in hydrazide was found to be fractional. Such fractional order in substrate concentration is due to the prior complex formation equilibrium between the reactants.

$$\begin{array}{llll} Tl^{3+} + \text{Hydrazide} & \rightleftharpoons & \text{Complex} & K_c \\ \text{Complex} & \rightarrow & Tl^{+} + \text{Intermediate} & k_1 \\ Tl^{3+} + \text{Intermediate} & \rightarrow & Tl^{+} + \text{Products} & \text{Fast} \end{array}$$

Scheme-I

The Michealis-Menten plots of 1/k_{obs} *vs.* 1/[hydrazide] were linear with an intercept in support of the complex formation. Therefore, in agreement with the results obtained the mechanism of the reaction can be represented as in **Scheme-I**. Equation 2 gives the rate according to **Scheme-I**. Since, total [Tl^{3+}] exists in the form of free [Tl^{3+}] and the complex (eqn. 3) therefore, the [Tl^{3+}] free is given by eqn. 6. The overall rate law is now expressed by eqn. 7 and the pseudo-first order rate constant kobs, by eqn. 8.

$$\text{Rate} = k_1\,[\text{Complex}] = k_1K_c\,[\text{Hydrazide}]_{free}\,[Tl^{3+}]_{free} \tag{2}$$

$$[Tl^{3+}]_{total} = [Tl^{3+}]_{free} + [\text{Complex}] \tag{3}$$

$$[Tl^{3+}]_{total} = [Tl^{3+}]_{free} + K_c\,[\text{Hydrazide}]\,[Tl^{3+}]_{free} \tag{5}$$

$$[Tl^{3+}]_{free} = [Tl^{3+}]_{total} / (1 + K_c\,[\text{Hydrazide}]) \tag{6}$$

$$\text{Rate} = k_1K_c\,[\text{Hydrazide}]\,[Tl^{3+}]_{free} \tag{7}$$

$$k_{obs} = k_1K_c\,[\text{Hydrazide}] / (1 + K_c\,[\text{Hydrazide}]) \tag{8}$$

Rate law 8 is verified by plotting 1/k_{obs} against 1/[Hydrazide] at four different temperatures and from the slopes and intercepts of these plots the values of k_1 and K_c were calculated and are given in Table-9.

The effect of H^+ and Cl^- concentrations on the reaction is due to the protonation of hydrazides[9] and different chloro-complexes of thallium(III) present in the solution. Hydrazides are known to be protonated in acid medium according to eqn. 9. Therefore, total [Hydrazide] can be expressed by eqn. 10 and thereby the fact that there was no effect of

$$RCONHNH_2 + H^+ \rightleftharpoons RCONHNH_3^+ \qquad K_H \tag{9}$$

Free [Hydrazide] by eqn. 12. Since the rates of reaction decreases as the [H^+] increases, free hydrazide is the active species. This is in support

$$[\text{Hydrazide}]_{total} = [\text{Hydrazide}]_{free} + [\text{Hydrazide}]_{protonated} \tag{10}$$

$$[\text{Hydrazide}]_{total} = [\text{Hydrazide}]_{free} + K_H\,[\text{Hydrazide}]_{free} \tag{11}$$

$$[\text{Hydrazide}]_{free} = [\text{Hydrazide}]_{total} / (I + K_H\,[H^+]) \tag{12}$$

of ionic strength on the reactions indicating one of the reactants is neutral. Thallium(III) forms strong complexes with Cl^- of the formula $TlCl_n^{3-n}$ where n is the number of chlorides complexes with thallium(III) as represented in equilibrium 13 to 16. The values of respective stability constants[10] are $K_1 = 1.38 \times 10^8$, $K_2 = 3.98 \times 10^{13}$, $K_3 = 6.02 \times 10^{15}$ and $K_4 = 1.0 \times 1018$ mol^{-1} dm^3. The presence of 3.0×10^{-2} mol dm^{-3} Cl^- concentration (which is the minimum [Cl^-] used in the present study) all the

$$T1^{3+} + Cl^- \rightleftharpoons TICl^{2+} \qquad K_1 \tag{13}$$

$$TlCl^{2+} + Cl^- \rightleftharpoons TlCl_2^+ \qquad K_2 \tag{14}$$

$$TlCl_2^+ + Cl^- \rightleftharpoons TlCl_3^+ \qquad K_3 \tag{15}$$

$$TlCl_3 + Cl^- \rightleftharpoons TlCl_4^+ \qquad K_4 \tag{16}$$

Thallium(III) will exists as $TlCl_2^+$ and its concentration can be expressed by eqn. 17. The $[TlCl_2]^+_{free}$ can now be given by eqn. 19 where, $\beta_1 = K_3/K_2 = 151$ and $\beta_2 = K_4/K_3 = 166$, further, using eqns. 18 and 19 the concentrations of $[TlCl_2]^+_{free}$, $TlCl_3$ and $TlCl_4^-$ were calculated at different Cl^- concentrations and

$$[Tl^{3+}]_{total} = [TlCl_2^+]_{total} = [TlCl_2^+]_{free} + [TlCl_3] + [TlCl_4] \qquad (17)$$

$$[TlCl_2^+]_{total} = [TlCl_2^+]_{free}\ (1 + \beta_1[Cl^-] + \beta_2[Cl^-]^2) \qquad (18)$$

$$[TlCl_2^+]_{free} = [TlCl_2^+]_{total}\ /\ (1 + \beta_1[Cl^-] + \beta_2[Cl^-]^2) \qquad (19)$$

compared with the change in rate constant as the chloride ion concentration varied. The concentration of both of $[TlCl_2^+]_{free}$ and $TlCl_3$ parallel the values of rate constants as $[Cl^-]$ changes but the order $[Cl^-]$ is -1.5, which makes $[TlCl_2^+]$ free as the only active species.

$$TlCl_2^+ + \text{Hydrazide} \rightleftharpoons \text{Complex} \qquad K_c$$

$$\text{Complex} \rightarrow RCONNH + TlCl_2^- + H^+ \qquad k_1$$

$$RCONNH + H_2O + TlCl_2^+ \rightarrow RCOOH + N_2 + 2H^+ + TlCl_2^- \qquad \text{fast}$$

where R = C_7H_7 for *p*-toluic acid hydrazide

Scheme-II

The mechanism considering $TlCl_2^+$ of oxidant and free hydrazide of the substrate as the active species can now be represented by **Scheme-II** with respective rate law and the expression for the pseudo-first order rate constants by eqns. 20 and 21. The rate law (eqn. 12) was verified by plotting $1/k_{obs}$ against 1/[hydrazide] and $1/k_{obs}$ against $[H^+]$ which were found to be linear. From the slopes and intercepts of these plots the values of K_c and K_H were determined. The values of K_c are

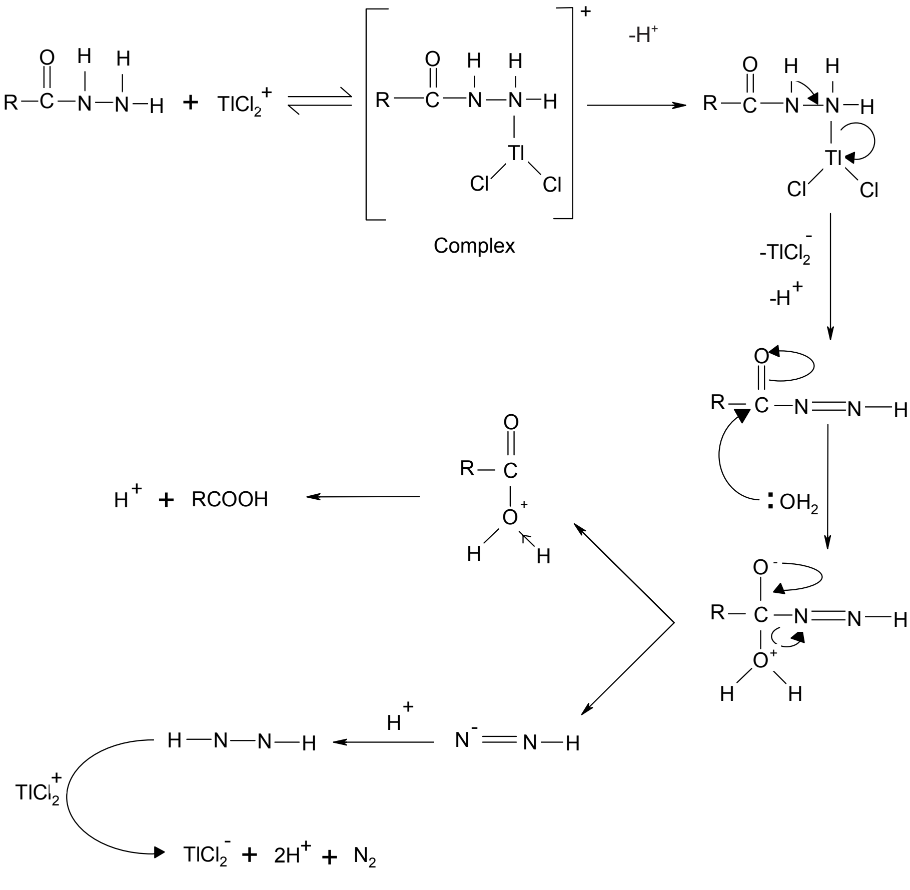
$$\text{Rate} = \frac{k_1K_c[\text{Hydrazide}]_{total}[TlCl_2^+]_{total}}{(1+K_c[\text{Hydrazide}])\ (1+K_H[H^+])\ (1+\beta_1[Cl^-]+\beta_2[Cl^-]^2)} \qquad (20)$$

$$k_{obs} = \frac{k_1K_C[\text{Hydrazide}]_{total}}{(1+K_c[\text{Hydrazide}])\ (1+K_H[H^+])\ (1+\beta_1[Cl^-]+\beta_2[Cl^-]^2)} \qquad (21)$$

given in Table-9 and those of K_H were found to be 13 and 16 $mol^{-1}\ dm^3$ for *p*-toluic acid hydrazide. The electrophilic character of $TlCl_2^+$ among the thallium(III) chloro-complexes is highest thus making it the reactive species. The detailed mechanism involves electrophilic substitution on the nitrogen of the hydrazide with the formation of N-Tl bond, which decomposes in the subsequent step with, direct two-electron transfer from hydrazide to thallium to give an intermediate followed by fast steps (**Scheme-III**). Such N-Tl bond formation has been postulated during thallium(III) oxidation of nitrogen[11] containing compounds.

TABLE-9
VALUES OF K_C AND k_1
[HCl] = 0.1 mol dm^{-3}, [$HClO_4$] = 0.1 mol dm^{-3}, [Tl^{3+}] = 3.0 × 10^{-3} mol dm^{-3},
I = 0.3 mol dm^{-3} in 50 % v/v 1,4-dioxane

Temperature (ºC)	K_C (mol^{-1} dm^3) [p-t H]	$k_1 \times 10^{-4}$ (s^{-1}) [p-t H]
15	14.93	3.57
20	14.63	5.00
25	14.70	7.14
30	14.85	14.20



R = C_7H_7 for *p*-toluic acid hydrazide

Scheme-III

The activation parameters, with respect to slow step, k_1, $\Delta H^{\#}$ (KJ mol^{-1}), $\Delta G^{\#}$ (KJ mol^{-1}) and $\Delta S^{\#}$ (JK^{-1} mol^{-1}) were found to be 43.76, 93.41 and -166.60, respectively for *p*-toluic acid hydrazide. Considerable decrease in the entropy of activation is due to formation of more ordered transition state as shown in **Scheme-III**. The mechanism involves neutral hydrazide as the active substrate thus the reaction is unaffected by the change in the ionic strength. The increase in 1,4-dioxane content in the reaction medium decreases. The rate such an effect of the solvent is due to the stabilization of the complex formed between reactants[12] in a medium of low relative permittivity.

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REFERENCES

1. (a) A.G. Lee, Chemistry of Thallium, Elsevier, England, p. 296 (1971); (b) A.G. Sykes, Advanced Inorganic Chemistry and Radio Chemistry, p. 153 (1967).
2. (a) R.J. Ouellette, in ed.: W.S. Trahanovsky, Oxidation in Organic Chemistry, Part B, Academic Press,p. 140 (1973); (b) A. Mckillop and E.C. Taylor, *Endevor.*, **35**, 88 (1976).
3. H. Paulsen and D. Stoye, in ed.: J. Zabicky, The Chemistry of Amides, Wiley, London, p. 515 (1970).
4. A.I. Vogel, Textbook of Quantitative Chemical Analysis, Longman, New York, edn. 5, p. 66 (1989).
5. M.S.P. Rao, R. Kalavathi, T.S. Rao and P. Sunita, *Oxid. Commun.*, **20**, 552 (1997) and the references there in.
6. G.S. Gokavi and J.R. Raju, *Polyhedron*, **6**, 1721 (1987).
7. (a) A. Mckillop, J.D. Hunt and E.C. Taylor, *J. Am. Chem. Soc.*, **93**, 4918 (1971); (b) R.N. Butler, G.J. Morris and A.M. O'Donohue, *J. Chem. Res.*, 61 (1981); (c) E.C. Taylor, R.L. Robey and A. Mckillop, *Angew. Chem. Int. Ed. Engl.*, **11**, 48 (1972); (d) E.C. Taylor, R.L. Robey and A. Mckillop, *J. Org. Chem.*, **37**, 2797 (1972); (e) A. Silveria, M. Angelastro Jr., R. Israel, F. Totino and P. Williamsen, *J. Org. Chem.*, **45**, 3522 (1980).
8. A.I. Vogel, Textbook of Practical Organic Chemistry, ELBS and Longman Group, edn. 4, p. 1125 (1975).
9. (a) K. Kazo, T. Hirakazo, K. Hisashi and T. Zenzo, *Chem. Pharm. Bull.*, **11**, 797 (1963); (b) P. V. Krishnarao, M.S. Frank and A.K. Ramaih, *React. Kinet. Cata. Lett.*, **9**, 59 (1978); (c) P.V. Krishnarao, M.S. Frank and A.K. Ramaih, *Indian J. Chem.*, **16A**, 418 (1978); (d) A.K. Ramaih, M.S. Frank, G. Baburao and P.V. Krishnarao, *Indian J. Chem.*, **18A**, 416 (1979).
10. A.G. Lee, The Chemistry of Thallium, C. Elsevier, London, p. 48 (1971).
11. (a) J.D. Mckillop Hunt, R.D. Naylor and E.C. Taylor, *J. Am. Chem. Soc.*, **93**, 4918 (1971); (b) R.N. Buttler, G.J. Morris and A.M. O' Donohue, *J. Chem. Res.*, 61 (1981).
12. E.S. Amis, Solvent Effects on Reaction Rates and Mechanisms, Academic Press, New York (1966).

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