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Solvent and Catalyst Effects on the Complexation of Toluene with $Cr(CO)_6$

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Summary. The effect of 8 solvents on the rate as well as the yields of complexation of toluene with $Cr(CO)_6$ has been studied. It has been found that the intensity of boiling has a profound effect on the rate of complexation in some cases (when *n*-hexanol, cyclohexanone or diglyme is used as solvent). The rates of complexation are highest in these cases, but a considerable extent of decomposition results in lower yields. Butyl acetate, dibutyl ether and decalin have been found to be the most feasible solvents. Additionally, 27 different catalysts have been tested for the complexation of toluene in decalin solution, their effect being quantified by rate constants and the isolated yields of the reaction. The rate constants have been obtained from the rate of CO evolution and vary from $6.6 \cdot 10^{-5}\,s^{-1}$ for formic acid to $6.5 \cdot 10^{-4}\,s^{-1}$ for ethyl acetamidomalonate. Cycloalkanones proved to be more efficient catalysts than acyclic ketones with a close boiling point. Lactones are more efficient than esters, both cyclic and acyclic ketones, and diesters, all having a similar boiling point.

Keywords. Arenetricarbonylchromium Complexes; Rapid Synthesis; Solvent and Catalyst Effect.

Lösungsmittel- und katalytische Effekte bei der Komplexierung von Toluol mit $Cr(CO)_6$

Zusammenfassung. Es wurde der Effekt von 8 Lösungsmitteln auf Komplexierungsgeschwindigkeit und Ausbeute der Komplexbildung von Toluol mit $Cr(CO)_6$ untersucht. Dabei wurde festgestellt, daß die Intensität der Erhitzung beim Sieden in einigen Fällen einen wesentlichen Effekt auf die Komplexierungsgeschwindigkeit hat (bei *n*-Hexanol, Cyclohexanon und Diglyme). Die Komplexierungsgeschwindigkeit ist in diesen Fällen die größte, die bereits beträchtlich einsetzende Zersetzung ergibt aber geringere Ausbeuten. Butylacetat, Dibutylether und Decalin erwiesen sich als die günstigsten Lösungsmittel. Außerdem wurden 27 verschiedene Katalysatoren für die Komplexierungsreaktion in Decalin als Lösungsmittel getestet und ihre Effizienz durch Geschwindigkeitskonstanten und isolierbare Ausbeute charakterisiert. Die Geschwindigkeitskonstanten wurden aus der Entwicklung von CO berechnet; sie liegen zwischen $6.5 \cdot 10^{-5}\,s^{-1}$ für Ameisensäure bis zu $6.5 \cdot 10^{-4}\,s^{-1}$ für Ethylacetamidomalonat. Cycloalkanone erwiesen sich als die besseren Katalysatoren gegenüber acyclischen Ketonen vergleichbaren Siedepunkts. Lactone sind effektvoller als Ester, cyclische sowohl als auch acyclische Ketone und Diester mit ähnlichen Siedepunkten.

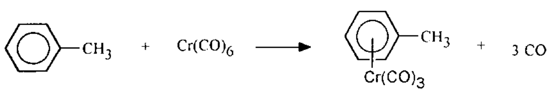
Introduction

Various solvents were used for the complexation of arenes with $Cr(CO)_6$. The most frequently employed ones are decalin, dibutyl ether, diglyme, 1,2-dimethoxyethane, dioxane, dibutyl ether/*THF* (5:1 – 10:1), etc. [1], but no comparison of these solvents has been made. As catalysts of the complexation, *THF* [2], α-picoline [3] and pyridine [4] were used. In our previous papers [5–7], the catalytic effect of different esters, ketones, acids, etc. on the course of arene complexation was described.

The goal of this work was to compare different solvents as complexation media and to gain an insight of the effect of intensity of boiling on the reaction rate. The main aim was to characterise the catalytic effect of various substances by rate constants and yields of the complexation, and to select the catalyst most favourable from the synthetic point of view.

Results and Discussion

The reaction of toluene with $Cr(CO)_6$ (Scheme 1) was chosen as the model process to assess the catalytic properties of the selected compounds.



Scheme 1

In order to be able to follow the course of the reaction, we designed an apparatus (Fig. 1), which allows to measure the volume of CO evolved. By plotting CO volume vs. time, we observed the behaviour illustrated in Fig. 2.

The steep increase of volume in the beginning of the curves corresponds to thermal expansion of the system before regular boiling is reached. Further course of the gas evolution is usually regular; exceptions being the cases where autocatalytic decomposition of the product occurs. However, even in cases like that there is a part of the curve that is not influenced by the decomposition (as it usually starts lateron during the progress of the reaction) and from which conclusions may be drawn. Thus the regular course is described best by a first order rate law

$$kt = \ln [a/(a - x)]$$

where a = the molar amount of CO corresponding to 3 CO fixed in $Cr(CO)_6$, x = molar amount of CO evolved during the time t, and k = rate constant.

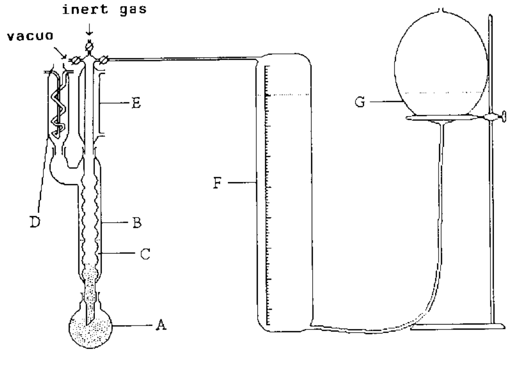


Fig. 1. The apparatus used for complexation. A – reaction flask, B – anti-sublimation condenser [5], C – cooling liquid, D – condenser of the cooling liquid, E – condenser of volatile components of the reaction mixture, F – calibrated cylinder, G – vessel for the liquid displaced from F (the vessel is moved down during the course of the reaction to equalise the levels in order to read the CO volume at atmospheric pressure)

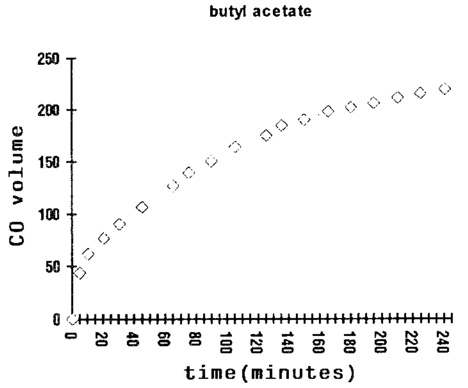


Fig. 2. The dependence of CO volume versus time. The steep increase of volume in the beginning of the reaction corresponds to thermal expansion of the system. After five minutes, regular boiling was reached and the reaction mixture started to yellow. This point has been considered as zero point for the calculation of kinetic parameters

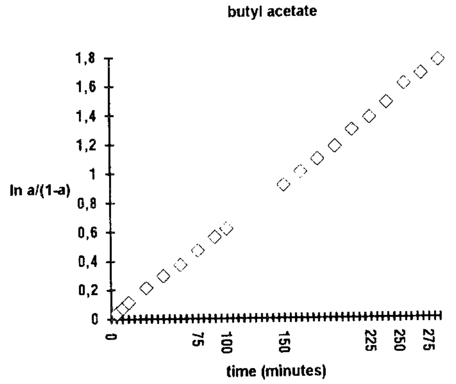


Fig. 3. The dependence of ln $a/(1-a)$ *vs.* time, obtained from the data depicted in Fig. 2

On the basis of the presumed mechanism discussed below a second order kinetics would be expected for the cases where substances with ligand properties, and hence catalytic activity, are present. However, we came to equal results applying a simple first order rate law and a second order rate law adapted for the fact that the concentration of the compound with catalytic properties is constant. We concluded that even in the cases where the concentration ratio of $Cr(CO)_6$ and the catalyst is as low as 1:3, the actual kinetics is of pseudo-first order, as the concentration of the catalyst does not change during the course of the reaction (Fig. 3).

However, even if we assume that the influence of eventual decomposition on the rate constants obtained is minimised to a reasonable extent, the data should be treated more or less as qualitative. Moreover, we found that the intensity of boiling influences the rate significantly. An experiment proved that it was not the effect of temperature itself: when a reaction mixture was heated without antibumping granules over five degrees beyond its boiling point, the CO evolution rate was about ten times lower than when the same mixture boiled with granules at a temperature of its boiling point. The explanation may consist in the fact that the reaction is reversible and, during regular boiling, the CO expulsion is much more effective than in the case of overheated mixture with CO escaping only from the level of the liquid. Hence, more effective CO expulsion shifts the equilibrium to the product regardless of the lower temperature. At a vigorous reflux, the CO expulsion is probably efficient to such an extent that the rate of the reverse reaction becomes negligible, allowing

Table 1. Complexation of toluene with $Cr(CO)_6$ in various solvents. Effect of the bath temperature on the rate of the reaction. (T bath temperature, S_k standard deviation, r correlation coefficient, w isolated yield, t reaction time)

Solvent	b.p.	T_1 (°C)	$k_1 \times 10^6$ (s^{-1})	S_{k1} (%)	r_1	t_1 (min)	w_1 (%)
		T_2 (°C)	$k_2 \times 10^6$ (s^{-1})	S_{k2} (%)	r_2	t_2 (min)	w_2 (%)
butyl acetate	125	181	8.6	6.6	.9913	240	19
		230	53	2.8	.9922	240	25
cyclohexanone	155	212	75	1.7	.9964	180	21
		263	310	1.7	.9982	90	17
dibutyl ether	142	200	42	3.1	.9944	240	15
		239	27	2.0	.9949	240	23
n-hexanol	157	217	260	4.5	.9766	175	51
		285	420	4.8	.9822	80	69
diglyme	162	213	9.6	5.9	.9697	240	6
		243	170	6.7	.9825	110	38
decalin	189–191	274	27	1.7	.9950	240	13
		291	28	2.2	.9926	240	15
n-heptane	99	143	0.8	32.4	.3463	240	0
1,4-dioxane	101	180	7.8	1.9	,9920	240	6

thus for being described by the first order rate low. In order to assess the influence of the intensity of boiling on the reaction rate, we have carried out experiments where the particular system has been exposed to two bath temperatures: one sightly above the boiling point, at which the boiling has been weak, and another one – usually about forty degrees higher, the boiling being vigorous. These experiments could help us to choose a solvent in which the error caused by the low stability of the bath temperature (±2 °C) would not cause a significant change of the rate constant. The results are summarised in Table 1.

As it can be seen, the rate of complexation is highly dependent on the bath temperature in solvents like butyl acetate, 1-hexanol, cyclohexanone, diglyme. The different measure of the dependence among particular solvents might perhaps he connected with different CO solubility in these liquids.

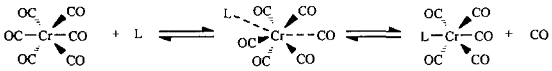
For the comparison of the catalyic activity we chose decalin as reaction medium for several resons: The rate constants measured in declain solutions are the least temperature dependent ones and therefore the errors due to bath temperature changes (±2 °C) should be small. The reaction time required is short with the extent of decomposition being reasonably low. The purification (as well as recycling) of decalin is convenient and it is easy to separate from the reaction product by passing through silica (see Experimental). A broard range of potential catalysts was chosen for testing in decalin solution and the results are given in Tables 2 and 3.

Again the general trend can be observed that higher bath temperature and hence more vigorous boiling results in higher reaction rates. The low difference in the case of *THF* might be caused by the low boiling point of *THF* and as the lower bath temperature was approximately the same for all experiments, it could be still high enough to cause more vigorous boiling with *THF* than in other experiments, where the additive had a higher boiling point. The rate constants were in the range of

Table 2. Catalytic effect of various substances on the complexation of toluene with $Cr(CO)_6$ in decalin. (T bath temperature, S_k standard deviation, r correlation coefficient, w isolated yield, t reaction time)

Catalyst	b.p. (°C)	T (°C)	$k \times 10^6 (s^{-1})$	S_k (%)	r	t (min)	w (%)
ethyl formate	54	282	88	1.1	.9980	240	36
butyl formate	106-7	285	120	3.0	.9831	240	57
ethyl acetate	77	285	73	1.1	.9981	240	48
butyl acetate	125	285	210	2.5	.9944	240	98
n-hexyl acetate	168-70	283	150	1.9	.9956	165	59
butyl butyrate	164-5	277	200	2.5	.9968	105	44
diethyl oxalate	185	283	190	2.1	.9967	120	51
methyl malonate	180-1	284	190	1.8	.9966	165	76
ethyl acetamido-malonate		279	650	2.7	.9977	40	40
methyl succinate	200	281	150	1.8	.9971	150	61
2-butanone	80	281	180	4.4	.9850	195	59
2-heptanone	149-50	278	130	.9	.9986	240	72
cyclopentanone	130-1	286	200	1.1	.9995	70	40
cyclohexanone	155	284	210	4.4	.9943	85	13
γ-butyrolactone	204-5	281	310	2.3	.9953	120	74
δ-valerolactone	219-22	280	250	.5	.9998	240	72
formic acid	100-1	270	66	1.9	.9955	240	15
acetic acid	116-17	283	230	2.9	.9943	135	34
propionic acid	141	282	420	2.9	.9975	40	4
2-butanone/acetic acid (40:3)	83	283	180	2.2	.9959	180	76
diethylene glycol	244	281	400	4.8	.9753	70	32
ethylene glycol	196-8	278	290	3.5	.9937	55	19
diglym	162	282	190	2.3	.9975	40	15
THF	67	282	110	3.3	.9822	240	67
acetonitrile	82	284	270	3.9	.9863	120	74
2-methyl chromone		280	200	1.1	.9989	120	55
xantone		281	170	.8	.9992	165	61

$6.7 \cdot 10^{-5}$ to $6.5 \cdot 10^{-4}$ implying the catalytic activity accordingly. However, as has been mentioned previously, this comparison includes not only influences of the catalyst structure but also the effect of temperature, to which the difference between, for example, ethyl and butyl acetate can be ascribed: an ethyl acetate-decalin mixture has a lower boiling point than the mixture of butyl acetate with decalin of the same ratio. Therefore the rate constant for the butyl acetate mixture is higher than for ethyl acetate. The relatively high rate constant for ethyl acetamidomalonate is very probably due to the complex decomposition which in this case is present from the very beginning of the reaction and its influence was not eliminated by considering the regular part of the reaction course. The other cases, where the difference in boiling points is small or they are too high to influence the boiling point of the mixture at all, the data allow us to treat the constants as measures of catalytic activity resulting from the substance's structure. Thus the activity of acetonitrile is higher than that of ethyl acetate; however, a certain extent of product decomposition occurs towards the end of the reaction in the case of acetonitrile, causing consistently lower yields. An interesting feature is the higher activity of cyclic substances compared to that of their acyclic analogs. In general, cyclic ketones are more active than acyclic ones, lactones are more efficient than simple esters. This could be ascribed to the steric crowding in the crucial step of the reaction which is presumably the substitution of CO for *L* (*L* being the catalyst) (Scheme 2).



Scheme 2

To support the proposed mechanism, we attempted to prepare the presumed intermediate – the complex $L\mathrm{Cr(CO)_5}$. Heating of a solution of chromium hexacarbonyl in butyl acetate (which, in presence of toluene, affords 90% of toluene tricarbonyl chromium after 12 hours) led to decomposition after barely perceptible yellowing of the mixture. No complex, besides chromium hexacarbonyl, was detected. However, irradiation of a solution of chromium carbonyl in ethyl acetate by UV light provided an intensively yellow solution of an unstable substance (characterised by IR and UV spectra) which, after addition of touene and two hours of reflux, afforded 25% yield of toluene tricarbonyl chromium. A comparative experiment, in which a solution of chromium hexacarbonyl and toluene in ethyl acetate was heated for several hours, gave no detectable amount of toluene complex. We presume that the yellow substance was $\mathrm{(EtOAc)Cr(CO)_5}$, relying on UV and IR spectra and also on the evidence from the literature [10] where analogous complexes

Table 3. Catalytic activity of various substances in complexation of toluene with $\mathrm{Cr(CO)_6}$ in decalin and the influence of different bath temperatures (T bath temperature, S_k standard deviation, r correlation coefficient, w isolated yield, t reaction time)

Catalyst	T_1 (°C) T_2 (°C)	$k_1 \times 10^6$ (s^{-1}) $k_2 \times 10^6$ (s^{-1})	S_{k1} (%) S_{k2} (%)	r_1 r_2	t_1 (min) t_2 (min)	w_1 (%) w_2 (%)
ethyl formate	283	88	1.1	.9980	240	36
	235	67	3.6	.9777	265	35
butyl acetate	285	210	2.5	.9944	240	98
	241	100	.6	.9994	300	96
cyclopentanone	286	200	1.1	.9995	70	40
	242	180	5.1	.9922	95	19
γ-butyrolactone	281	310	2.3	.9953	120	74
	242	50	3.1	.9876	330	40
δ-valerolactone	280	250	.5	.9998	240	72
	242	95	4.2	.9843	250	38.5
THF	282	110	3.3	.9822	240	67
	241	110	3.2	.9870	270	73
acetonitrile	284	270	3.9	.9863	120	74
	245	100	.4	.9998	240	58

have been described. In [11], practically the same approach is used to prepare arenetricarbonylchromium complexes.

Lactones were found to be even more efficient catalysts than diesters (which are more efficient than simple esters). However, from the synthetic point of view, both diesters and lactones have a great drawback. Due to their high boiling points, it is rather difficult to separate them from the reaction product. Thus the longer reaction time required in the case of e.g. butyl acetate (3–4 hours compared to 1–2 hours for diesters) is outweighed by the easy removal of ester by evaporation from the decalin solution using a rotary evaporator.

It might be expected that there should be some relationship between the catalytic activity and basicity of the catalyst, at least in analogous structures. However, no clear-cut correlation has been observed. Lactones were found to be more basic than esters [7] what is in agreement with our findings, but δ-valerolactone is more basic than γ-butyrolactone, and the opposite behaviour was found at complexation. But once again, this could be ascribed to higher steric requirements of the former.

Conclusions

1. The reaction rates of complexation of toluene with $Cr(CO)_6$ are highly dependent on boiling point of the reaction mixture. In some cases, also bath temperature exhibits a great influence presumably via influencing the intensity of boiling.

The highest rates have been observed in *n*-hexanol, diglyme and cyclohexanone as solvents, but the yields in the last two cases are lowered due to considerable extent of product decomposition during the reaction and isolation. In *n*-hexanol, the yield was the greatest but the OH group probably has a catalytic effect and therefore, we chose decalin as the most feasible solvent for the study of effect of potential catalysts. The easy isolation of the product and convenient purification of the solvent was taken into consideration as well (see Experimental).

2. The highest rate constants at catalytic complexation have been found for ethyl acetamidomalonate, propionic acid and diethylene glycol. On the other hand, the highest yields have been obtained in reactions catalysed by butyl acetate, dimethyl malonate, 2-heptanone, γ-butyrolactone, δ-valerolactone, acetonitrile and a mixture of 2-butanone with acetic acid (40:3). From the synthetic point of view, simple esters are more convenient due to the easy separation from the reaction product.

3. It is usually necessary to examine more catalysts to optimise a complexation. Thus it appears [6] that butyl acetate is an excellent catalyst for benzene derivatives, ethyl formate works best for condensed polycycles (e.g. 80% yields have been achieved in complexation of naphthalene) and heterocycles [9], and acetic acid is the best catalyst in the complexation of ketones [8].

Experimental Part

Chromium hexacarbonyl was sublimed through a layer of microwave-oven-dried alumina. All solvents were distilled prior to use. Decalin was purified by passing through 4 × 2.5 cm column of microwave-oven-activated silica.

Non Catalysed Complexation of Toluene with $Cr(CO)_6$

The apparatus (Fig. 1) was evacuated and filled with argon. Then 0.5 g (2.27 mmol) of $Cr(CO)_6$, 0.6 ml (6.82 mmol) of toluene and 70 ml of a solvent were placed in the flask and the apparatus was evacuated and filled with argon four times. The reaction mixture was heated for 4 h (or less when the calculated CO volume was reached). After cooling the mixture down, the solvent was removed by evaporation or, when decalin was used, by flash chromatography on SiO_2 (40–80 mesh, 7 × 2.5 cm). Decalin was washed down by petroleum ether, leaving the complex adsorbed on silica. Benzene was used to elute the product which was then crystallised from a benzene-petroleum ether mixture. The yields listed in Tables 1–3 are yields of isolated products calculated on the basis of reacted $Cr(CO)_6$.

Catalysed Complexation

The experiments were realised under the same conditions as those of non catalysed complexation. The molar ratio of toluene: $Cr(CO)_6$:tested substrate was 3:1:3 with the exception of the experiment when ethyl formate was used. Then the ratio was 3:1:9.

Preparation of η^6-Touluenetricarbonylchromium by UV-Irradiation of Chromium Carbonyl Solution

A solution of chromium hexacarbonyl (0.2 g, 0.9 mmol) in 60 ml of ethyl acetate was placed in a Schlenk tube, equipped with a magnetic stirring bar, and the tube was then evacuated with cooling by liquid nitrogen. During the irradiation by a 400 W medium-pressure Hg lamp, the solution turned intensively yellow. The CO formed during the process was removed in four regular intervals by an oil pump. After 4 h, 2 ml (12.5 mmol) of toluene was added and the resulting solution was heated to 80 °C for 2.5 h. Evaporation of the solvent, subliming-off the unconsumed chromium hexacarbonyl and recrystallisation from ethyl acetate-isohexane mixture afforded 0.05 g (25%) of η^6-toluentricarbonylchromium. The ^{1}H-NMR spectra and microanalysis of the product were in agreement with literature.

An analogous experiment, with toluene being present in the ethyl acetate solution during irraidiation, afforded 0.07 g (35%) of the product. The mentioned intensively yellow intermediate of the presumed structure $(EtOAc)Cr(CO)_5$ was characterised in the following manner: The solution of chromium hexacarbonyl from the previously described experiment was irradiated for 4 h and the UV spectrum was measured. It exhibits a symmetrical band at 442 nm. Another part of the solution was evaporated and the IR spectra in nujol of the solid residue was measured (cm^{-1}): 1990 (CrC=O), 1900 (EtOC=OCr), 1040 (C–O–C).

Acknowledgements

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